The renaissance of graphene-related materials in photovoltaics with the emergence of metal-halide perovskite solar cells

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Broader Context
Since the first isolation of graphene, a single layer of carbon atoms arranged in a hexagonal lattice, due to its unusual properties, efficiently conducts heat and electricity and is nearly transparent, graphene-related materials (GRMs) have been widely investigated over a wide range of optoelectronic applications. Recent developments in perovskite solar cells (PSCs), metal halide perovskite semiconductors have become one of the most promising materials in the field of photovoltaics, have generated broad interest including the exploitation of GRMs towards efficient, low-cost and stable PVs. GRMs excel in adaptability and tenability. The doping of heteroatoms into a sheet of GRMs can tune their physical, optical, and electrical properties allowing in this way their adoption into a PSC and its exploitation as dopants inside the absorber and as an electron or hole transporting layer depending on their energy band alignment with the absorber. Additionally, in PSCs, the highly conductive GRMs have been also utilized as transparent and flexible bottom and top electrodes. Moreover, the use of GRMs has a great impact on the enhancement of the long-term stability of PSCs, functioning as a shielding layer against humidity ingress; contributing to the opening of the commercialization of this new generation of solar cells.
Abstract
The electronic and material properties of graphene have been explored in a number of electronic and optoelectronic devices among them the organic and metal–halide perovskite solar cells. At present, graphene based technology is considered to have the greatest potentialities for applications. More over graphene related materials offer graphene characteristics and also the freedom to tune their chemical, electrical and physical properties through doping and functionalization processes. On the other hand, the metal halide perovskite solar cells is the most rapid advanced photovoltaic technology with exponential increase of theirs certified power conversion efficiency. The most pronounced disquiet is the stability of these devices, which has limiting their practical applications and their commercialization. The synergy of properties of metal halide perovskite semiconductors and GRMs have recently progressed and contributed towards the realization of highly efficient perovskite solar cells that demonstrated impressive operational stabilities. In this work, we review the progress have been made in the specific field of graphene based metal halide perovskite solar cells since 2013. The impact of exploitation of graphene and GRMs into this technology is multiple, since resulted in the progress of higher quality perovskite crystal construction to the fabrication of more stable, flexible and high performed devices.
Introduction

Increasing energy consumption is an inevitable consequence of the global economic development. The need for unlimited clean energy sources such as sunlight, wind, rain, waves and geothermal has increased. Almost 27% of the total global electricity capacity is generated using renewable energy sources. Sustainability and green energy are two of the most important keywords of modern societies when referring to energy sources. The requirement for sustainable and renewable energy resources is redirecting our energy suppliers, towards more efficient and low-cost production and conversion technologies. In line with this priority, the need for efficient, high performance solar cells is becoming vital since represent the fastest growing technology, the cheapest and easiest way to generate clean energy. The International Energy Agency’s Photovoltaic Power System Programme latest report\(^1\) found that 75 gigawatts of solar were installed globally in 2016 bringing the total global installed photovoltaic capacity to approximately 303 gigawatts. That equates to producing 375 billion kilowatt-hours of solar power each year, which represents 1.8 percent of the electricity needs of the planet. Cost efficiency is the dominant driving force for the establishment of solar cells as the main renewable electricity generator. Photovoltaic (PV) module pricing demonstrates a Moore law tendency. Solar modules pricing has made radical progress moving from $300 per watt in 1956, to $10 per watt in the 1990s, to $0.40 per watt today. The dominance of solar cells as the principal renewable energy source will necessitate implementation of abundant, solution processed, environmental benign and rapidly scalable technologies. Organic\(^2\) and organic-inorganic nanomaterial\(^3\) based solar cells are expected to be among them.

Among the different photovoltaic technologies reported to date,\(^4\) third generation cells have recently experienced a major breakthrough with the introduction of perovskite solar cells (PSCs). Hybrid metal halides PSCs have opened a very popular research field in materials science. Over the recent years, organic – inorganic PSCs are rapidly emerging as the most promising photovoltaic technology and have made great strides due to hybrid perovskite materials’ intriguing physical, electronic properties\(^5,6\) such as direct and tunable band gap, relatively low exciton energy (~ 20 meV) at room temperature,\(^7\) high charge bipolar conductivity (10\(^{-2}\) – 10\(^{-3}\) S cm\(^{-1}\)),\(^8,9\) high absorption coefficient (10\(^4\) cm\(^{-1}\)),\(^10\) low trap state density and large diffusion lengths in the micrometer to tens of micrometer range.\(^11\) The lead or tin halide PSCs are the state of the art of this technology and has attracted the scientific community’s attention because can be
processed from solution and yet demonstrate properties described in solid state physics textbooks. The high degree of freedom during the synthesis of the hybrid perovskite crystals, offers a variation of materials and crystal structures, resulting in 3D, 2D or 1D materials with tunable energy band gaps, thus well adapted for solar cell applications. PSCs have reported impressive leaps; within few years their PCEs have exceeded 22% performance and are already considered as an effective alternative photovoltaic technology. For efficient PSCs with internal quantum efficiency close to 100% over a wide absorption spectrum under standard testing conditions, the reported short current density ($J_{sc}$) has almost reached (22-23 mA/cm$^2$) the theoretical limits (23.8 mA/cm$^2$) for perovskite compounds. More work must be done for the theoretical limit of the open circuit voltage ($V_{oc}$) (1.32 eV) to be reached. Therefore, one of the hot topics for PSCs community is how to further push forward the device photovoltage and thus the device performance. Semiconducting halide perovskites are based on the ABX$_3$ perovskite crystal structure, (see Figure 1) where A is an organic cation such as methylammonium (CH$_3$NH$_3$, MA) or formamidinium (NH$_2$CH=NH$_2$, FA), B is a metal (mainly Pb or Sn), and X is a halogen atom (mainly I, Cl, Br).

![Figure 1. Methylammonium cation (CH$_3$NH$_3^+$) occupies the central A site surrounded by 12 nearest-neighbour iodide ions in corner-sharing PbI$_6$ octahedra. Reproduced with permission from Ref. 18 (Copyright© 2015, Nature Publishing Group).](image)

The characteristics and properties of this structure (chemical composition and orientation) are vital parameters that define the overall photovoltaic performance of the solar cell. The MA ion is placed in a cage surrounded by four PbX$_6$ octahedra. In this setup the occupation and the
orientation of the organic amino cations determine the spacing between the inorganic layers. The organic part is interchangeable thus MA part can be changed by FA. This substitution tunes the energy bandgap between 1.56 and 1.48 eV and leads to more stable cells. From the other hand the PCE of FAPbI₃ is lower than this one of CH₃NH₃PbI₃ (MAPbI₃) cells. MA and FA phases can be combined, (FAPbI₃)₁₋ₓ(MAPbBr₃)ₓ, and PCEs of the order of 18% has been reported in cells that demonstrate the advantages of both of the phases.¹⁹ Tin – based perovskites such as CH₃NH₃SnI₃ have attracted attention due to their lead free and thus low toxic character. Despite their more environmental friendly character these devices demonstrate lower PCEs. PSCs are solid-state hybrid organic – inorganic devices initially adopted the architecture of dye sensitized solar cells (mesoscopic architecture),¹³ while by removing the mesoscopic layer can also be considered as thin-film solar cells (that under the standard architecture follow the n-i-p structure,²⁰ whereas the p-i-n form is called the inverted structure) (see Figure 2).²¹,²²

![Figure 2. Schematic diagram showing (a) the mesoscopic, (b) the planar normal and (c) planar inverted PSC architectures and the most commonly used materials for each layer of each architecture.](image)

In general, a transparent rigid or flexible substrate functions as an electron – selective (mesoscopic or n-i-p configuration) or as a hole selective (p-i-n configuration) electrode is deposited, followed by the electron transport layer (ETL) (mesoscopic or n-i-p) or the hole transport layer (HTL) (p-i-n) interlayers. Between the interlayers the metal halide perovskite semiconductor is placed. For the most efficient photo-generated carriers collection the conduction band (CB) of the perovskite should be energy paired with the CB of the ETL whereas the valence (VB) of the perovskite should be energetically matched with the VB of the HTL. Moreover for the efficient collection of the photo-generated carriers the work function (WF) of the anode should matched with the CB of the ETL and the WF of the cathode should be energetically be aligned with the VB of the HTL.
The PV performance of PSCs is very much regulated by the electrical, physical properties of the light harvester, the HTL and ETL material consist the solar cell. The desired properties from these building blocks, include high absorption coefficient, fast extraction rates from the light harvester into the HTLs & ETLs, fast transportation from the HTL & ETL towards the respective electrodes and finally electron & hole blocking capabilities by the HTL and ETL respectively. The most popular selected transparent conductive electrode (TCE) in mesoscopic PSCs is the fluorine doped tin oxide (FTO) while in both the planar normal and planar inverted architectures is the indium tin oxide (ITO). Both TCEs despite their low sheet resistance (R_s) (few tens of Ω/sq) and their high transparency (90% in visible) exhibits poor bending capabilities, low abundance and are of high cost. These are drawbacks that prohibit the use of ITO and FTO TCEs in flexible electronic applications. In mesoscopic architecture the titanium dioxide blocking layer (bl-TiO_2) and the mesoporous titanium dioxide (mp-TiO_2) is the most often combination of selected ETL material. However this material (bl-TiO_2/mp-TiO_2), requests high processing temperatures that forbids its application with flexible substrates. However, to date, the high record certified PCEs in this technology have achieved using this aforementioned approach. From the other hand in planar configuration, Phenyl-C61-butyric acid methyl ester (PCBM) is the choice of the majority of the researchers. This organic material exhibits low processing temperatures and are of low cost. However, its low conductivity and stability issues prohibit its further exploitation in PSCs. The perovskite / HTL interface plays an important and multiple role regarding the performance and the stability of PSCs. The HTL materials strongly affect among others, the crystallization of the perovskite semiconductor (in the planar inverted architecture) and the kinetic dynamics of the photogenerated carriers. The most studied HTLs in PSCs are 2,2’,7,7’-tetrakis(N,N-di—p-ethoxyphenylamino)-9-9’-spirobifluorene (spiro – OMeTAD), poly(3-hexyl-thiophene) P3HT, poly(triarlyamine) (PTAA) and the Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). Apart their attractive characteristics, these HTL materials exhibited some drawbacks that should be tackled in order to be established as dominate HTL materials. Among these disadvantages are including the low hole mobility (spiro – OMeTAD and PTAA), low achieved PCEs (~ 10% in P3HT based systems), the hygroscopic and acidic nature (in case of PEDOT:PSS) that are detrimental on device performance. The thermal properties of the selected HTL also very much affect the thermal stability of the PSCs. Thermal degradation of the HTL is a critical challenge to be
addressed. Another challenge is the shielding protection capabilities the HTL can provide to the perovskite from moisture, water molecules (mesoscopic and n-i-p) and UV radiation to intrude the light harvesting material (p-i-n). Further improvements are necessary for the PSCs commercialization mainly regarding the mitigation of the hysteresis, prohibiting light soaking effects, more understanding of the hybrid perovskite crystallization processes. Reproducibility issues during the fabrication of these cells still exist and must be overcome. Other challenges include long-term stability and sustainability issues.²⁶

Since the first isolation of graphene in 2004²⁷, graphene related materials (GRMs) have led to substantial progress in both fundamental and applied physics, make them the rising star materials due to their extraordinary properties.²⁸,²⁹,³⁰ GRMs are low cost abundant materials that are easily processed in low temperatures, theirs exceptional electrical & physical properties are easily tuned through functionalization/doping with heteroatoms and are compatible with flexible substrates and printing electronics applications. Until now a number of GRMs have been studied and be applied in organic solar cells, such as (chemical vapor deposited) CVD – grown, isolated/free standing, single layer, multi-layer, nanoflakes, nanoribbons, nanoplatelet graphene and so on.³¹ Recent developments in PSCs have generated broad interest, including the use of GRMs (using spin coating, vacuum filtration, chemical vapor deposition, electrophoretic deposition, spray-coating, Langmuir horizontal deposition method and hot pressing deposition techniques) in PSCs as a promising low cost solar cell technology. The GRM based lead or tin halide PSCs follow the progress of the PSCs in general (see figure 3 – number of published papers reporting the use of graphene in the field of perovskite solar cells).
Figure 3. Bar-plot showing the increasing number of published articles (red) and total citations (blue) containing the expression “Perovskite Solar Cells” and “Graphene” either in the title or in the abstract during the period 2013 and 2018. In the left part of the diagram are presented the number of papers that have already been reviewed in the literature while in the right side of the diagram are shown the papers that have not been reviewed in the literature before this work. Source: Scopus bibliographic database (December 2017).

The last extended reviews on GRM based PSCs was published at the beginning of 2016. Based on the progress of the field, the challenges that should be faced and be addressed regarding the performance, stability and scalability of GRM based PSCs, a new extended review article, that also is more focused in graphene and the device engineering & performance, is necessary in order to update the scientific community with the new developments. The main focus has been paid in applications of modifications of graphene oxide (GO) into various building blocks of PSCs as HTL or ETL or an interlayer that facilitated the charge extraction & fast transfer from the active layer into HTL or ETL or from the interlayers to the respective electrodes. The electrical, physical and mechanical properties of the GO derivatives are fully controlled through its functionalization with different electronegativity heteroatoms. GO demonstrates relatively low sheet resistance ($10^2 - 10^3$ $\Omega$/sq, high transparency in visible (more


than 80% at 550 nm), is solution processed and can be deposited into various rigid and flexible substrates using facile spin coating techniques. Its main disadvantage is its insulating properties that can be tackled mainly using reduction processes leading to electrical conductive reduced graphene oxide (rGO).\textsuperscript{35} rGO have been demonstrated as highly capable in the field of organic photovoltaics\textsuperscript{36,37} and has also started to be an excellent option as TCE in the field of PSCs as well. Following the research has been implemented in other solar cell technologies; rGO has been applied in PSCs in its pure form, or has employed after its functionalization with a heteroatom or has been used as a composite with a polymer or other two-dimensional (2D) materials.

In this review article we capture the all the developments and works that has been implemented from 2013 until now in the emerging field of graphene & GRM based PSCs. In part I the application of GRMs as both top and bottom electrodes in PSCs is presented. In part II the utilization of GRMs as ETLs or as interlayers between the perovskite and the selected ETL is discussed in mesoscopic and planar PSC configurations. In part III the published works related the application of GRM as HTL or interlayers between the perovskite semiconductor and the HTL are discussed. In part IV the exploitation of GRM-Perovskite hybrid composites as active layer of PSCs is also summarized. Finally in part V the challenges and perspectives of the PSCs that should be addressed by GRMs are presented.

**Graphene Based Materials as Electrodes in PSCs**

The full synergy of the unique properties of lead halide perovskite semiconductors with low temperature solution processed and flexible transparent bottom or top electrodes is a priority in the field of flexible PSCs. The scientific community is focused to introduce electrode materials that demonstrate high bending tolerance and at the same time generate PCEs (> 17%) comparable to the ITO (a brittle transparent conductive oxide) as bottom electrode and gold (Au) or aluminum (Al) or silver (Ag) as the top electrode of PSCs. Table 1 summarizes the record results that has been reported in the literature regarding the utilization of GRMs as electrodes in both mesoscopic and planar PSCs.

**Mesoscopic PSCs**
Bottom Electrodes

M. Batmunkh et al.\textsuperscript{38} exploiting the low cost, the chemical stability, the unique mechanical, electrical and optical properties of solution processed graphene, demonstrating its potential as TCE in flexible PSCs. Furthermore they tested the feasibility of the fabricated transparent conductive graphene films (TCGFs) to be employed within semiconducting oxide scaffolds and compact layers in metal halide PSCs. After chemical processing, thermal annealing and decoration with Au NPs, the TCGFs showed $R_s$ as low as 1.96 $\Omega\text{sq}^{-1}$ and transmittance ($T_r$) of 42.3\% (see figure 4a & b). Since there is a tradeoff between high $T_r$ and low $R_s$ (see figure 4c), the authors by controlling the adopted deposition and doping processes demonstrated TCEs with 86.6\% $T_r$ and 15.7 $\Omega$/sq $R_s$. The Au – NPs decorated TCGFs employed as TCEs in mesoscopic $\text{MAPbI}_3$-$\text{Cl}_x$ PSCs. The photovoltaic parameters changed in a different way as a function of the $R_s$ and the $T_r$ of the TCGF electrode. More particularly the $V_{oc}$ was not affected by the thickness of the TCE, whereas the fill factor (FF) was increased as the sheet resistance was decreasing. However, the short circuit current density ($J_{sc}$) was not optimized in the same way as the values of the FF. The $J_{sc}$ value was increasing with the thickness of the TCE up to a point, beyond which due to the $T_r$ lowering, its values were decreased. The record PCEs were achieved for TCEs $R_s$ of 3.08 $\Omega$/sq @ 55\% transmittance, yielding values of 0.62\%. 
Figure 4. (a) $R_s$ vs. thickness of the graphene films prepared from four different structures; (b) $R_s$ and $T_r$ (at $\lambda = 550$ nm) of selected TCGFs with different thicknesses; (c) comparison of $R_s$ as a function of transmittance (at $\lambda = 550$ nm) between AuNPs–RGO films and other studies. Reproduced with permission from Ref. 38 (Copyright © 2016, The Royal Society of Chemistry).

Top Electrodes

The long electron and hole diffusion lengths the perovskite semiconductors demonstrate, has permitted the demonstration of free of ETL and HTL PSCs. The degradation of the noble metals employed as top electrodes in PSCs should be also tackled. K. Yan et al.\textsuperscript{39} motivated by the instabilities caused by the doped spiro - OMeTAD and the metal electrode materials, realized an HTL-free mesoscopic PSC that employed GRM based top electrode. The authors studied the impact of the utilization of single layer graphene (SG) and multilayered graphene (MG) top
electrodes in the performance of MAPbI₃ based PSCs (see figure 5a&b). The main findings were the higher & fastest hole extraction the MG cathode secured compared to the SG cells. This was attributed to the Schottky rectifying characteristics of the perovskite / MG graphene electrode interface, that facilitated the hole extraction and simultaneously the electron blocking. As a result the PCE reached values higher than 11% (~ 11.5%) and the FF obtained a high outcome of 70%, which was comparable to HTM based PSC (see figures 5c-f).

Figure 5. Cross-section view of (a) single layered graphene (SG) and (b) of multilayered graphene (MG) based PSCs (scale bar: 1 μm). (c) J–V curves and (d) IPCE spectra of SG PSC and MG PSCs. (e) Voc and (f) Jsc under on–off illumination for SG and MG PSCs. Reproduced with permission from Ref. 39 (Copyright© 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Planar PSCs

Bottom Electrodes

H. Sung et al.⁴⁰ exploited CVD single layered graphene to be used in combination with a thin layer (~ 2nm) of molybdenum trioxide (MoO₃) as a flexible transparent bottom electrode instead of the state of the art ITO. The necessity to employ a thin layer of MoO₃ on top of the CVD
graphene has been obliged in order to enhance the wettability (and thus achieved better formation of PEDOT:PSS HTL onto the graphene’s surface) and engineer the energy levels of graphene. The hole doping the MoO$_3$ film induced to graphene, resulted the tuning of the latter’s work function from 4.23 to 4.72 eV. This facilitated the hole transport and collection by the graphene bottom electrode. The authors as a reference PSC utilized an ITO/MoO$_3$ based cells. The introduction of an optimum thickness (~2nm) of MoO$_3$ layer (see figure 6a&b), contributed to the lowering of the glass/graphene/MoO$_3$/PEDOT:PSS roughness (~ 0.29nm) compared to the roughness the glass/ITO/MoO$_3$/PEDOT:PSS demonstrated (~1.95nm). The lower surface roughness the glass/graphene/MoO$_3$/PEDOT:PSS film exhibited, facilitated the hole transportation & collection by the bottom electrode (see figure 6e&f). Additionally the employment of the graphene/MoO$_3$/PEDOT:PSS combination resulted in the better crystallization of the MAPbI$_3$ semiconductor. XRD measurements revealed larger & more oriented crystal grain sizes resulted in the case of graphene/MoO$_3$/PEDOT:PSS systems compared to the ITO/MoO$_3$/PEDOT:PSS based substrates. The record PCEs achieved was 17.1% which was comparable with the ITO/MoO$_3$ systems (see figure 6c&d).

Great effort is done to replace ITO with a new conductive and transparent material in visible – infrared (IR) region of the solar spectrum, demonstrating high mechanical flexibility, with high chemical stability and also to be able to be uniformly deposited without forming pinholes onto the selected substrate. J.H. Heo et al.$^{41}$ proposed the use of AuCl$_3$ – doped (p-doped) single layer graphene as TCE in planar inverted PSCs. Through the doping process, the WF and the conductivity of the p-doped graphene electrode was tuned in order to optimize the performance of the PSCs. The $R_s$ of the p-type doped graphene electrode was decreased whereas its $T_r$ was lowered as a function of molar concentration of AuCl$_3$. The PCE of the MAPbI$_3$ planar inverted PSCs was increasing up to a maximum concentration of AuCl$_3$ (10 mM). Beyond this concentration value, the decreased $T_r$ of the electrode overruled the lowering of its $R_s$ and the PCE started to decrease. The record PCEs was 17.9% (42.6% increase compared to the un-doped graphene electrode based reference MAPbI$_3$ inverted PSCs) when the $R_s$ and the $T_r$ of the p-doped graphene electrode were $70 \ \Omega$/cm$^2$ and $\sim 85\%$ respectively. In addition the AuCl$_3$-doped graphene TCE based MAPbI$_3$ PSCs exhibited good stability under continuous light soaking at 1 Sun in ambient conditions.
The high demand for portable, high performance, low cost fabricated and flexible energy sources for optoelectronic devices are continuously growing to date. One of the key issues of high performance flexible PSCs is the performance of its photovoltaic parameters as a function of the bending conditions impended to the transparent electrode. GRM based electrodes are appearing in the recent literature as a very promising solution for flexible PV applications. J.H. Heo et al.\textsuperscript{42} proposed the introduction of 3-aminopropyl triethoxysilane (APTES) adhesion promoter between the GRM based electrode and Polyethylene terephthalate (PET) substrates in order to promote their chemical bonding. As a result the PSCs fabricated on top of GRM based electrode / APTES / PET TCE substrates exhibited excellent bending stability, maintaining its initial PCE over 90% after 100 bending cycles for bending radius R \( \geq 4 \text{ mm} \). Contrary when the ITO/PET or AuCl\textsubscript{3} – GR/PET TCE based PSCs experienced similar bending stress tests theirs PCEs were deteriorated to 30% and \( \sim 20\% \) of their initial PCE values. The demonstrated high mechanical strength under severe bending conditions, was attributed to the AuCl\textsubscript{3} – GR/APTES/PET TCE strong bonding between the PET and the GRM based electrode that did not permitted the de-attachment of the latter from the flexible substrate. Moreover in order the GRM based R\textsubscript{s} to be further lowered and approach this one exhibited by ITO based electrodes, graphene electrodes were chemically n-doped with AuCl\textsubscript{3}. Finally the authors demonstrated high performance, high mechanical strength (ultra-flexible) planar inverted MAP\textsubscript{bI}\textsubscript{3} & FAPbI\textsubscript{3-x}Br\textsubscript{x} GRM based TCE PSCs demonstrated the highest PCE of 16.1\% and 17.9\% respectively at 1 Sun condition.

J. Yoon et al.\textsuperscript{43} proposed the transfer of single layer of CVD graphene, doped with few nanometers thick MoO\textsubscript{3}, on a thin polyethylene naphtalate (PEN) substrate. The p- type induced graphene doping by the MoO\textsubscript{3} was not only increased the graphene’s conductivity but also improved its wettability that allowed the most uniform deposition of the HTL onto it. Even though the PCE of the graphene based PSC (with MAPbI\textsubscript{3} absorber) was lowered (due to higher R\textsubscript{s} of the MoO\textsubscript{3}/graphene/PEN resistance in respect to ITO/PEN), from 17.3\% to 16.8\%, the flexibility was improved. The binding stability of the graphene based PSCs was impressive since after 1000 bending cycles with bending radius of 4mm, the PCE remained more than 90\% of its initial value. In contrary the ITO/PEN based PSCs PCE degraded faster and more severely, since its PCE reduced to 25\% of its initial value under similar bending tests (see figure 6g-j).
**Figure 6.** The dependence of PCE with the thickness of MoO$_3$ layer for (a) graphene electrodes and (b) ITO electrodes. J–V curves for state of the art (c) G-M2 and (d) ITO-M1 PSCs under one sun illumination conditions measured via reverse (blue) and forward (black) bias scan. (e) The dependence of $R_s$ and MoO$_3$ thickness for graphene and ITO based electrodes. (f) $T_r$ of graphene and ITO with/without 2 nm thick MoO$_3$ layers. Reproduced with permission from Ref. 40 (Copyright© 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (g) Normalized PCEs of the Gr-Mo/PEN and ITO/PEN PSCs measured after 1000 bending cycles with different bending radii. (h) Normalized PCEs as a function of bending cycles at a standard bending radius of 4 mm for the Gr-Mo/PEN and ITO/PEN PSCs. Inset image presents the Gr-Mo/PEN PSC bent at a bending radius of 4 mm. Evolution of the J–V curves of the (i) ITO/PEN and (j) Gr-Mo/PEN devices throughout 1000 bending cycles with a fixed radius ($R = 4$ mm). Reproduced with permission from Ref. 43 (Copyright© 2017, The Royal Society of Chemistry).

**Top Electrodes**

The fabrication of transparent, conductive CVD graphene top electrode in perovskite (large band gap) / silicon (low band gap) tandem solar cells demonstrate advantages over other reported top electrodes (metal electrodes, silver nanowires mesh, carbon nanotubes, PEDOT:PSS composite layers) have tested in similar configurations: high $T_r$, high conductance, deposition...
onto perovskite without degradation of the below deposited organic HTL. F. Lang et al.\textsuperscript{44} utilized graphene based TCEs into tandem perovskite / silicon solar cells in order to boost their performance (see figure 7a). The authors managed to demonstrate that CVD graphene top electrode demonstrated similar charge collection performance & light management, even at long wavelengths, as gold electrodes in planar perovskite solar cells, lower FFs due to the higher graphene electrode $R_s$ over the corresponding Au ones. The graphene / perovskite solar cells transmitted 64.3\% of the incident light at 860 nm (see Figure 7b). The graphene/perovskite solar cell (top cell, large band gap semiconductor) operated as an optical filter that absorbed all the radiation with $\lambda < 775$ nm, into a four terminal tandem configuration. The radiation with $\lambda > 775$ nm was harvested by the bottom heterojunction amorphous / crystalline silicon solar cell (low band gap). The efficiency of the tandem solar cell amounted to 13.2\%. These results were similar to respective four terminal tandem devices that used as the top electrode the state of the art ITO.

![Figure 7](https://example.com/f7.png)

**Figure 7.** (a) Device schematic of a four terminal tandem solar cell consisting of a top graphene based PSC and an amorphous/crystalline silicon bottom solar cell. (b) External and internal quantum efficiency spectra of the graphene (red) and Au (black) electrode respectively. Reproduced with permission from Ref. 44 (Copyright© 2015, American Chemical Society).

P. You et al.\textsuperscript{45} demonstrated a semitransparent planar normal PSCs fabricated using laminated stacked CVD graphene as top transparent electrodes for the first time. The PCE was optimized by improving the conductivity of the graphene electrodes and the contact between the top graphene electrodes and the spiro-OMeTAD deposited on top of the perovskite films. The
record performance was attained with double-layer (2L) graphene electrodes exhibiting PCEs of 12.02% ± 0.32% and 11.65% ± 0.35% from the FTO and graphene sides, respectively, which are relatively high compared with the reported semitransparent perovskite solar cells. Apart from the high PCE for graphene top electrode device another highlight is its excellent mechanical flexibility and facile preparation compatible with printing or roll to roll process.

Tandem solar cells consisting from a combination of a high and a low band gap absorber result in PCEs that outperform the respective state of the art single junction ones. Recently, PCEs of 28% have been reported. An essential part of such configurations is the deposition of a top electrode that exhibits high transparency in VIS and NIR regimes. Ideal properties of such an electrode apart of its T, are its low Rs and its compatibility with the below deposited organic HTL. F. Lang et al.46 towards the realization of high performance perovskite tandem solar cells, proposed the utilization as a transparent, flexible and high conductive electrode, a single layer CVD deposited graphene film in combination with a metal grid. The graphene electrode Rs was lowered as an effect induced by the Spiro – OMeTAD (interface passivation, hole selectivity and graphene doping) and the incorporation of the metal grid (optimization of grid spacing as a function of the graphene layers stacked should be performed in order the FF to be increased). These combined actions reduced the graphene Rs by 24% compared to bare CVD graphene samples. The impact of the selected electrode configuration (graphene or Au) was reflected by the overall MAPbI3 based single junction solar cell performance. More particularly the glass/FTO/TiO2/MAPbI3/spiro-OMeTAD/graphene/metal grid/polymer stack based PSCs demonstrated PCEs of the order of 6.02% compared to 2.3% the glass/FTO/TiO2/MAPbI3/Au based PSCs exhibited.

The most intelligent way to deal with the quantities of produced CO2 is its conversion into novel solid-state materials such as carbon nitride, lithium cyanamide and GRMs. W. Wei et al.47 reacted potassium, a very important metal for soil health and animal nutrition, with CO2 to form a new type of 3D graphene sheet. The authors tuned the time of reaction in order mainly to improve the electrical properties of the fabricated carbon based sheets. The tendency was the Rs to decrease with the reaction time. The 3D honeycomb structured graphene (3DHG) were 2.8 nm thick and consisted of 10 or less graphene sheets. The Raman and XPS measurements indicated that the fabricated 3DHG was rich of defects (strong D peak at 1580 cm⁻¹) and the main
component is sp²-bonded carbon (81.4%). The high conductivity (Rₛ as low as 3.97 kΩ/ sq) and the Tₑ of the potassium assisted fabricated 3DHG challenged the authors to exploit them as top electrode in HTM free planar normal MAPbI₃ PSCs. To improve the interface, the 3DHG was introduced into the solution of perovskite precursors. The record PCE (10.06%) was recorded for the 48 hours duration reaction 3DHG based PSC. This was mainly attributed to the lowest Rₛ the increase in the synthesis time 3DHG electrode film resulted.

In summary, the graphene based electrodes demonstrated their use and potential as ITO or gold/aluminum replacement candidates. GRM electrode based PSCs showed properties that the corresponding state of the art materials cannot demonstrate such as flexibility and ability to tune its electrical properties.

**Table 1.** Photovoltaic parameters of PSCs incorporating graphene based material electrodes.

<table>
<thead>
<tr>
<th>Architecture / Absorber</th>
<th>Electrode</th>
<th>Electrode Material</th>
<th>PCE (%)</th>
<th>Other Benefits</th>
<th>ΔPCE (%)</th>
<th>Ref.</th>
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<tr>
<td>Mesoscopic / MAPbI₃Clₓ</td>
<td>Bottom</td>
<td>rGO decorated with Ag NPs on glass</td>
<td>0.81</td>
<td>N/A</td>
<td>30</td>
<td>(rGO) M. Batmunkh et al. 2016 [38]</td>
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<tr>
<td>Mesoscopic / MAPbI₃</td>
<td>Top</td>
<td>Multilayered Graphene on glass</td>
<td>11.5</td>
<td>N/A</td>
<td>11</td>
<td>(single layer graphene) K. Yan et al. 2015 [39]</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>Bottom</td>
<td>CVD graphene / MoO₃ bilayer on glass</td>
<td>17.1</td>
<td>N/A</td>
<td>- 9</td>
<td>(ITO/MoO₃) H. Sung et al. 2016 [40]</td>
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<td>Planar Inverted / MAPbI₃</td>
<td>Bottom</td>
<td>AuCl₃ doped rGO on glass</td>
<td>17.9</td>
<td>N/A</td>
<td>55</td>
<td>(ITO) J.H. Heo et al. 2017 [41]</td>
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<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>Bottom</td>
<td>AuCl₃ doped CVD GR/APTES bilayer on PET</td>
<td>16.1</td>
<td>Bending tolerance</td>
<td>2</td>
<td>(ITO) J.H. Heo et al. 2017 [42]</td>
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<tr>
<td>Planar Inverted MAPbI₃</td>
<td>Bottom</td>
<td>CVD graphene doped with MoO₃ onto PEN</td>
<td>16.8</td>
<td>Bending tolerance</td>
<td>-3</td>
<td>(ITO/PEN) J. Yoon et al. 2017 [43]</td>
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Graphene Based Materials in the ETL of PSCs

To further increase the PCE and lifetime of the PSCs the flow of photo-generated electrons through the ETL should be precisely controlled and stabilized. One way to achieve this objective is to insert interlayers between the metal halide perovskite semiconductor and the electron transport layer. Graphene due to its exceptional electrical, optical and mechanical properties is an ideal material to fabricate such interlayers. Table 2 summarizes the record results that have been reported in the literature regarding the utilization of GRMs as ETLs, interlayer or dopants in mesoporous and planar PSCs.

Mesoscopic PSCs

The introduction of low temperature processing techniques compatible with flexible, low cost, solution processed electronics standards (processing in temperatures below 150 °C) is of high priority in order to boost the competitiveness of PSCs. The most commonly used ETL, TiO$_2$ metal oxide, request high temperatures (~ 500 °C) for their sintering/crystallization. These temperatures are forbidden, when flexible deposition substrates are requested (such as PET or malleable metal foils) by the specific application or the available budget. J.T.W. Wang et al.$^{48}$ proposed the incorporation of graphene / TiO$_2$ composites as ETL in mesostructured Al$_2$O$_3$ based mixed halide (CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$) solution processable PSCs. The nanocomposites of graphene with anchored TiO$_2$ NPs (diameter size of the order of 25 nm), required low temperature
processing (< 150 °C), in order to reach high charge mobilities, that makes them compatible with flexible substrates. The use of liquid phase exfoliated (LPE) graphene nanoflakes (size distribution from 0.1 to 1 μm, consisting from five graphene layers)/ TiO₂ within the ETL provided superior electron collection that led to PCEs up to 15.6%. This PCE was higher than the corresponding values of PSCs employed high temperature processed TiO₂ ETL. This improvement was attributed to the superior electrical properties of the graphene / TiO₂ composite. The record performance, for an optimized GO nanoflakes concentration within the blend of GO/TiO₂ (0.6 wt% above which graphene might directly tough the perovskite and degrades the PSCs performance due to creation of excess of recombination centers), was 15.7%. The higher performance of the cells incorporated the nanocomposites of graphene/TiO₂ was primary attributed to the lower energy barrier the electrons experienced in the interface during their transfer from the active layer to ETL. Secondly, the higher conductivity the graphene platform offered, created lower charge accumulation effects in the interfaces (the series resistance after the incorporation of graphene flakes was lowered from 10.1 to 4.3 Ohm cm⁻²), thus to less recombination and as a result to higher photovoltaic characteristics.

In PSCs the charge extraction time with the recombination & thermalization times are competitive parameters. A lot of research have been undertaken in order to improve the electron extraction time in PSCs that is too slow (0.4 – 0.6 ns) compared to the hot carrier thermalization time (0.4 ps) observed in these devices. Obviously, a large amount of the absorbed photon energy is wasted and a significant amount of charges are recombined. This relation between the extraction and thermalization times, is one of the obstacles for the further enhancement of the PSCs PCE, since generates high recombination rates (so limit the maximum possible Jₚ, FF) and lowers the achieved Vₜ (since a lot of energy is lost due to electron’s thermalization). Z. Zhu et al. with the introduction of graphene quantum dots (GQDs) as an interlayer between the perovskite and the ETL, demonstrated GQDs potential to function as a superfast electron tunnel that enhanced the PCE of PSCs. The deposition of GQDs (few layers of graphene but of tiny size of only 5-10 nm diameter) interlayer between the perovskite and the employed ETL (mp-TiO₂) lowered the electron extraction time (from GQD into TiO₂) from 260 – 307 ps to 90 – 106 ps. As a result the PCE of the GQDs based interlayer PSCs increased over these ones without, from 8.81 % to 10.15% (~ 15% enhancement). The faster extraction times, increased the probability of low energy photo generated electrons (generated by the utilization of visible photons) to be
injected into the ETL due to lower charge trapping probability. The GQD concentration, dispersed into the mp-TiO₂, affected the overall device performance and the record results were obtained for 0.5 mg/L inside the mp-TiO₂ layer. These findings showed the superior role of graphene as a bridge transfer link for the photo-generated electrons compared to other reported materials.⁵⁰,⁵¹

Mesoporous TiO₂ is the most commonly used ETL in PSCs demonstrating at the moment the highest record PCEs. Despite its excellent performance as ETL, its relative low electron mobility (0.1 – 4 cm² V s⁻¹) has triggered the research for alternative anode materials with superior electron mobility. One of the materials that have been investigated is the ternary oxide SrTiO₃ that its electron mobility equals to 5 – 8 cm² V s⁻¹. Although the energy band gap of the SrTiO₃ is similar to the TiO₂, the higher conduction band of the former provides a better energy level alignment with the MAPbI₃ semiconductor. Low recombination rates are also reported when SrTiO₃ is employed instead of TiO₂ due to its higher dielectric constant. Despite the high-obtained V₉₀ values (> 1 V) when mp - SrTiO₃ was exploited, the reported Jₛₑₜ values were inferior to the respective mp-TiO₂ ETL based cell. Following the work have been done in the graphene / mp- TiO₂ nanocomposites, C. Wang et al.⁵² proposed an effective way to improve the Jₛₑₜ in the mp- SrTiO₃ MAPbI₃ based PSCs, proposing the use of SrTiO₃ / graphene nanocomposites as an ETL. The record reported PCEs of the graphene / mp-SrTiO₃ ETL based PSCs were 10%. The use of the proposed nanocomposite instead of mp – SrTiO₃ produced much higher Jₛₑₜ (enhanced from 12.42 to 18.08 mA/cm²). According to the SEM images, the SrTiO₃ NPs (of various diameters from 5 – 65 nm) adhered onto the graphene flakes. This strong bonding was exploited to use graphene flakes as a highway for electron transportation and collection. The concentration of graphene within the SrTiO₃ very much affected the performance of the ETL within the device. The optimum results were obtained for 25 mg of graphene within the nanocomposite with SrTiO₃. Above this concentration the PSCs PCE was degraded due to (1) the formation of recombination centers due to the direct contact of graphene with the perovskite and (2) the lowering of the Tᵣ of graphene/ mp-SrTiO₃, as the graphene concentration increased, which resulted in the decrease of absorbance of CH₃NH₃PbI₃, eventually reducing the amount of photogenerated carriers. The PCE enhancement after the incorporation of graphene within the mp- SrTiO₃ was attributed to observed faster electron transfer, less charge recombination rates, better MAPbI₃ achieved crystallinity (larger perovskite crystal grains and
thus less trapping states) on top of graphene / mp-SrTiO$_3$ compared to on the mp-SrTiO$_3$ and to the enhanced absorption in visible of the nanocomposite ETL PSCs.

As previously discussed TiO$_2$ needs thermal annealing to properly operate as ETL. As a result of this thermal annealing, boundary regions are formed that degrade the demonstrated ETL conductivity due to scattering effects across these boundary regions. New ETL materials with improved electron transport properties are under investigation in order to lower the charge recombination rates due to charge accumulation and improve the charge collection due to higher demonstrated electron conductivities. G.S. Han et al.\textsuperscript{53} proposed the incorporation of an rGO/mp-TiO$_2$ nanocomposite ETL (~ 400 nm thickness) that exhibited superior electron transport properties compared to the bare mp-TiO$_2$ ETL. The recorded improved PCE (higher $J_{sc}$, $V_{oc}$ in an FTO/c-TiO$_2$/rGO-mp TiO$_2$/MAPbI$_3$/spiro-MeOTAD/Ag system) was attributed to the lower perovskite/HTL interfacial resistance, that improved the electron charge collection, as a result of the superb electrical conductivity of the rGO. The achieved improvements resulted as a function of the rGO concentration within the mp-TiO$_2$ film. The record PCE improvement (18%) was reported for an optimal rGO concentration of 0.4 vol.%. The optimum doping level of the mp-TiO$_2$ ETL with rGO, resulted in the enhancement of all the photovoltaic parameters: the $J_{sc}$ was enhanced from 19.6 to 21.0 mA/cm$^2$, the $V_{oc}$ has been increased from 0.86 to 0.91 mV and the FF has jumped from 66.8 to 70.8 %. The overall PCE has been improved from 11.5 to 13.5%. The further doping (with higher concentrations than 0.4%) of mp-TiO$_2$ with rGO led to PCE degradation due to the enhanced absorption the higher rGO concentration induced (the rGO absorbs in the wavelength range of 200 – 800 nm) and thus the lower light harvesting. The internal quantum efficiency (IQE) for the composite ETL system was ~ 7% higher than the mp-TiO$_2$ based PSCs. This was a clear indication of the improved collection efficiency of the nanocomposite based on PSCs. Accompanied with electrochemical impedance spectroscopy (EIS), the rGO/mp-TiO$_2$ nanocomposite films demonstrated smaller resistivity, higher electron transport (twice faster diffusion lengths) and reduced charge recombination (slightly longer recombination times) compared with that of mp-TiO$_2$ NPs. UPS measurements reconfirmed the better energy alignment the rGO immersion into the mp-TiO$_2$ provided (lower energy level of rGO compared to the conduction band of the mp-TiO2) to the HTL and thus the facilitation of the charge transfer from the perovskite and mp-TiO$_2$ to the rGO.
The low conductivity of the TiO$_2$ layers (compact and mesoporous) employed into the MAPbI$_3$ based mesoscopic PSCs forced the scientific community to introduce strategies to improve their electrical properties. T. Umeyama et al.\textsuperscript{54} proposed the utilization of rGO into both the bl- and mp- TiO$_2$ layers used in PSCs. As a result of the higher conductivity both layers demonstrated after the immersion of rGO, the PCE of the MAPbI$_3$ based PSCs increased by 40%; from 6.61% jumped to 9.3%. This PCE enhancement was attributed to the lower sheet resistances the perovskite/mp-TiO$_2$ and cp-TiO$_2$/FTO interfaces exhibited after the immersion of rGO (EIS measurements). The more balanced electron to hole mobilities, the lower series resistances and the most favorable energy alignment the graphene based TiO$_2$ layers introduced, facilitated the electron transfer and collection. As a result and after the optimization of the rGO concentrations into the bl-TiO$_2$ (0.15% wt) and into mp-TiO$_2$ (0.018% wt) the $J_{sc}$ was increased from 14.5 to 16.5 mA/cm$^2$ and FFs from 0.583 to 0.674.

A key issue that PSCs technology should address is the transporting time of the photo-generated carriers from the active layer into the ETL substrate. The existing demonstrating times (0.4 ns for electrons) are much longer than hot carrier cooling (~ 0.4 ps). As a consequence a large amount of converted photon energy is wasted in the thermalization process and in carrier trapping. A. Agresti et al.\textsuperscript{55} demonstrated the incorporation of lithium neutralized graphene oxide (GO – Li) as an interlayer between perovskite semiconductor and ETL in mesoscopic PSCs. The presented results underline how the WF tuning of graphene based material can provide optimized efficiency and improve the lifetime of the PSC. The PCE of the GO-Li based PSCs (11.1%) was enhanced by 12% compared to the mp-TiO$_2$ reference device, mainly due to (1) better energy alignment between GO – Li and the mp-TiO$_2$ ETL that secured more efficient electron transfer in terms of energy; (2) higher electron extraction rate; and (3) lower electron trapping due to mp – TiO$_2$ electron traps passivation from the GO-Li. All these improvements were reflected to the higher acquired $J_{sc}$ (increased by 10.5%) and FF (7.5%) values. More over the GO – Li based PSCs demonstrated longer operational stability due to the oxygen mp – TiO$_2$ oxygen vacancies (electron trapping sites) passivation induced by the GO-Li interlayer. Finally GO – Li inclusion contributed to the reduction of the hysteresis factor by 50% due to the improved interface properties (e.g. less electron trapping, faster electron transportation towards the ETL) the GO-Li cells demonstrated compared to the reference cells.
The development of new low temperature processed, high conductive and ultra-stable ETL materials, is among the current research priorities towards the commercialization of the perovskite solar cells. The most commonly employed ETL materials, TiO$_2$ and ZnO are disadvantaged due to their high temperature processing (500 °C) and low temperature demonstrated instabilities respectively. The aforementioned drawbacks motivated the work implemented by S. W. Tong et al.\textsuperscript{56} The authors proposed the use of a low processed mesoporous graphene/polymer (mp-GP) thermally composite as an ETL in high performance MAPbI$_3$ PSCs. The authors reported enhancement of the PCE compared to the reference graphene based devices of the impressive 48%; the PCE skyrocketed from 9.3% to 13.8%. The mp-GP ETL demonstrated high conductivity (due to graphene network, two orders of magnitude higher than the mp-TiO$_2$ ETL in the reference PSCs) and facilitated (1) the uniform MAPbI$_3$ deposition (through the large mp-GP porous, 100 – 400 nm sized); (2) the excellent crystallization of the on top spin deposited MAPbI$_3$ semiconductor (the wider pores in mp-GP scaffold allow larger perovskite crystals); and (3) the thermal stability of the overall mp-GP based PSCs (the mp-GP based device after a thermal annealing at 150 °C for 30 min, degraded its performance by only 12% whereas the graphene based PSCs degraded by 81%). The higher thermal stability of the mp-GP cells was attributed (1) to the shielding the mp-GP offered to the MAPbI$_3$ crystal from moisture; (2) to the high heat transmission of graphene and to its low isoelectric point. The authors demonstrated the importance of the mp-GP thickness on the overall device performance (the thinner mp-GP scaffold is the higher the perovskite absorption). The record photovoltaic performance achieved for 265 nm thick mp-GP. In order PCEs higher than 13% to be reached, further interface mp-GP/MAPbI$_3$ engineering needed. The authors modified the energy levels of the mp-GP ETL by the insertion of ultrathin Cs$_2$CO$_3$ coating at mp-GP/perovskite interface; as a result the WF of the mp-GP reduced from 4.4 to 4.13 eV and thus easier transportation of photogenerated electrons facilitated from the MAPbI$_3$ to ETL (lower recombination rate) due to lower energy barrier at the interface. Moreover the deposition of the thin film of Cs$_2$CO$_3$ not only affected the WF of the mp-GP but also lowered the contact resistance and increased the recombination resistance of the Cs$_2$CO$_3$/mp-GP interface.

Another candidate to serve as the ETL in PSCs is the Zn$_2$SnO$_4$ (ZSO) ternary metal oxide (TMO) since it demonstrates some features that make it quite attractive for this purpose. These characteristics are similar to these ones of the most common used ETL material, the anatase
TiO₂, but accompany with higher energy band gap (3.7 eV). Even more, the charge injection and electron diffusion efficiency of this material is much higher than that of the TiO₂ based ETLs. Porous ZSO exhibited excellent chemical stability for acid/base and organic solvents make it compatible with a great range of other materials used in the different building blocks of PSCs. Moreover, its synergy with rGO improves even more its optoelectronic properties. S. S. Mali et al.⁵⁷ reported the application of rGO grafted ZSO scaffold as an ETL towards high efficient PSCs. The authors fabricated rGO-ZSO ETL based MAPbI₃ and MAPb(IₓBr₁₋ₓ)₃(FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ PSCs that demonstrated improved PCEs in respect to the reference devices. The optimized device, MAPb(IₓBr₁₋ₓ)₃(FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅, exhibited PCEs higher than 17% which was 142% higher than the PCE of the reference (MAPI₃, ZSO) cells (7.38%). The rGO had a dual role since operated as: (1) a bridge for the electron transfer between the perovskite and ZSO nanofibers that facilitated the fast electron extraction (the extraction time was reduced from 6 ns to 1.39 ns) and (2) an excellent electron acceptor. Moreover, the authors studied the impact of rGO grafting onto ZSO nanofibers regarding the stability the respective PSCs showed under operational conditions. The rGO/ZSO based hybrid MAPb(IₓBr₁₋ₓ)₃ and double cation (FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ PSCs demonstrated an improved stability up to 500 minutes. This stability enhancement was attributed to low sensitivity the mixed halide perovskite has towards exposure to humidity, characteristic associated to their compact and stable structure.

Despite PSCs impressive PCE advancement, further improvements are necessary to advance their performance and enhance their operational stability. K. T. Cho et al.⁵⁸ studied the impact of the immersion of rGO flakes into the various building blocks of mesoscopic mixed (FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ PSCs. Depending on the rGO mixing layer, the impact of the rGO to the PSC characteristics varied drastically. The immersion of rGO flakes into lithium bistri fluoromethanesulfonimidate (Li-TFSI) treated mp-TiO₂ ETL resulted in a PCE enhancement compared to the control, free of rGO flakes, PSCs. More specifically, both the Voc and FF parameters were increased. These improvements were attributed to the passivation of traps due to the lithium treatment of the ETL and the fast electron extraction, within one ns, the rGO pathways provided. The rGO based ETL device demonstrated a record PCE of 19.5% compared to the 18.8% of the reference device.
Despite the low cost, simple production processes and tremendous increase in the demonstrated PCEs, there is a lot of work to be done in order to improve the air and thermal stability of the PSCs. The limited exhibited lifetime of PSCs under ambient conditions is mainly attributed to the hydrophilicity of the most common employed HTLs i.e. Spiro–OMeTAD and the metal halide perovskite active layer itself. These issues should be tackled in order this type of photovoltaic cells to meet the demanded stress standards set at the International summit on organic photovoltaic stability. A. Agresti et al.\textsuperscript{59} demonstrated the beneficial double role of GRMs in improving the PSCs PCE and stability. The authors suggested the simultaneous utilization of graphene flakes into the mp-TiO\textsubscript{2} and GO as a buffer layer between the active medium and the HTL. This strategy resulted in improved PCEs, reaching efficiencies of 18.2\%, owing to a significant improvement in the average values of $J_{sc}$ by 11.7\% and the FF by 4.3\% with respect to the GRMs free reference PSCs. These improvements were attributed to the facilitation of electron extraction from the PS into the mp-TiO\textsubscript{2} due to the dispersion of graphene flakes into the ETL. Moreover the addition of the GRMs it is beneficial for the long term stability of the PSCs i.e. the mp-TiO\textsubscript{2} /graphene flakes based cells retained more than 88\% of their initial PCE after 16 hrs of prolonged one sun illumination at the maximum power point (MPP). The mp-TiO\textsubscript{2}/graphene flakes & GO interlayer based on cells also exhibited improved thermal stability with respect to mp-TiO\textsubscript{2} / graphene flake based cells at 60 °C.

The PSCs success story is directly linked with the successful efforts of the scientific community to improve the morphology of the perovskite crystals, to simplify theirs fabrication process, to lower their costs and to optimize the interface engineering between the constituent building blocks. More particular, the interface engineering is a decisive parameter that determines the losses, and thus the achieved PCEs, due to charge recombination at the interface between the perovskite and the transporting layers. A fine tuning of interface and interlayer properties is mandatory to enhance the charge transport and extraction. Graphene and GRMs have shown their potential as ideal elements to tune the interface properties between the perovskite and the transporting layers. A. Agresti et al.\textsuperscript{60} showed that graphene and GRMs can play a pivotal role in tuning the interface engineering in perovskite solar modules (see figure 8a). The authors demonstrated improved photovoltaic performances and stabilities. This was realized when the ETL mp-TiO\textsubscript{2} was doped with graphene flakes and GO-Li flakes spin coated interlayer between the ETL and the perovskite was inserted (see figure 8b). The doping of the mp-TiO\textsubscript{2}
resulted in faster electron extraction rates from the perovskite active layer into the ETL mainly due to excellent electrical properties of graphene flakes. On the other hand the better energy alignment induced by the introduction of the GO-Li fakes interlayer between the perovskite and the ETL, contributed to the more efficient photo-generated electron collection. All these improvements resulted in the realization of GRM based PSC module with PCE of $\sim 12.6\%$ on an over 50 cm$^2$ active area at one Sun illumination conditions. The demonstrated PCEs were 9% higher in respect to the graphene free reference PSC module. This enhancement was mainly a result of higher achieved FF (by 8.8%). Notably, prolonged aging tests have shown the long-term (1630 hrs until the reference devices shown 20% drop of theirs PCE) stability of the PSC modules. In fact the graphene based PSC module retained the 82% of its PCE at the end of the shelf life test (see figures 8c-f). These results revealed that the dispersion of graphene flakes into the mp-TiO$_2$ enhanced the stability of high efficient GO-Li based PSC modules.

Figure 8. (a) Image of the large area perovskite solar module with 50 cm$^2$ active area. (b) J-V curves of the tested modules (reference module PSM-A, module with GO-Li interlayer PSM-B, module with graphene-doped mp-TiO$_2$ based PSM-C, module with GO-li interlayer and graphene in mp-TiO$_2$ PSM-D). Normalized (c) $V_{oc}$, (d) FF, (e) $I_{sc}$ and (f) PCE trends vs time extracted by 1 SUN I-V characteristics, periodically acquired during the shelf-life protocol (ISOS-D-1). Reproduced with permission from Ref. 59 (Copyright© 2017, American Chemical Society).

Planar PSCs
M.M. Tavakoli et al.\textsuperscript{61} proposed the incorporation of rGO scaffold (rGS) on top of which the MAPbI\textsubscript{3} semiconductor was deposited. The 3D rGS was deposited using electrophoretic process and its impact on the MAPbI\textsubscript{3} PSC’s performance was tremendous. The rGS based PSCs demonstrated superior PCE compared to the TiO\textsubscript{2}/perovskite cell, induced a PCE improvement by 38\% (the average PCE has jumped from 11.7 to 16.2\%). This PCE progress was due to the substantial enhancement of the $J_{sc}$ (by 19\%) and the FF (by 6\%) whereas the $V_{oc}$ was not affected by the incorporation of the rGS. The PCE enhancement upon the utilization of the rGS, was mainly attributed the higher quality MAPbI\textsubscript{3} crystallization (longer grain sizes), enhanced light trapping (higher EQE), facilitation of the photogenerated carriers transport (as TRPL and static PL measurements showed). Moreover the devices incorporating the rGS, showed almost no hysteresis effects and higher stability under ambient conditions.

High sensitivity to ambient conditions and significant photo-charging effect remain as bottlenecks for the further commercialization of metal halide perovskite solar cells. Recently has been reported the successful incorporation of solution processed GRMs into the device configuration to tackle the aforementioned challenges. G. Kakavelakis et al.\textsuperscript{62} studied the beneficial impact of the immersion of rGO into the PCBM ETL of planar inverted PSCs. More particularly the authors proposed the utilization of rGO as an additive into the PCBM for both the hybrid mixed halide CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3-x}Cl\textsubscript{x} and CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite absorbers based PSCs. It was firstly shown that the addition of rGO enhanced the electron conductivity of the PCBM by fivefold, causing the faster electron extraction (see figures 9n-p) from the perovskite absorber toward the ETL and leading to higher $J_{sc}$ (increased from 20.65 to 22.92 mA/cm\textsuperscript{2}) & FF values (from 65.3 to 65.8). Moreover rGO reduced the surface traps and passivated perovskite surface resulting to (1) the $V_{oc}$ enhancement (836 mV to 850 mV); and (2) the light soaking effect reducing by a factor of three. The photovoltaic performance of the rGO:PCBM PSCs was superior to the PCBM ETL based PSCs and the record PCE measured was of the order of 14.5\% for the hysteresis free MAPbI\textsubscript{3} absorber (an increase of 12.5\% in respect to the reference devices). The positive impacts of the rGO immersion into the PCBM were not only limited to these improvements but also prolonged the device stability, at an optimum rGO concentration into the PCBM, under illumination (for 120 hrs) in ambient conditions ( > 50\% RH). The improved stability was attributed to the enhanced fracture resistance of the composite rGO:PCBM demonstrated compared to the bare PCBM ETL. Also the passivation of the top
surface of the perovskite by the rGO also slowed down the photo-degradation of the overall PSC device.

E. Bi et al.\textsuperscript{63} engineered a nanostructured ETL that suppressed the diffusion of iodine and at the same time facilitated the photo-generated electrons faster extraction from the perovskite layer. The suggested nanostructured ETL placed between the perovskite and the metal electrode containing N – doped graphene, PCBM and carbon quantum dots (CQDs). The demonstrated ETL presented three times improved capability of blocking ions/molecules mitigation of that of conventional ETLs of the same thickness. The tested nanostructured ETL also slowed down the mitigation of Ag atoms from the electrode to the perovskite, which is another source of degradation. The nanostructured ETL based MAPbI\textsubscript{3} PSCs presented improved thermal and light stability (see figures 9j-m). Stabilized PCE of over 15% during thermal aging test at 85 °C for 500h or light soaking under 1.5G illuminations for 1000 h were demonstrated by sealed G-PCBM/CQDs ETL based planar inverted PSCs. The record PCE of G-PCBM/CQDs ETL based planar inverted PSCs was 17.0%.

The ideal ETL material should demonstrate some specific characteristics in order to further improve the PCE of the planar inverted PSC, such as: high electron mobility, suitable energy level matching of the ETLs’ conduction band (CB) with the CB of the perovskite semiconductor, suitable hole blocking capacity and chemical compatibility with the perovskite. E. Nouri et al.\textsuperscript{64} demonstrated the use of low cost and abundant GRMs in planar inverted MAPbI\textsubscript{3} PSCs. The authors, showed the successful and simultaneous application of GO and GO-Li as HTL and ETL interlayers. The performance of the demonstrated devices was further improved with the additional use of a thin layer of a Ti based sol that further improved the energy level alignment between perovskite and the Al electrode. All the layers of the demonstrated devices were spin coated (apart the deposition of the Al electrode). The record performance was achieved when both the GO and GO-Li/Ti-sol HTL and ETL were employed in respect to the GO & Ti-sol HTL and ETL based reference devices. The PCE enhanced by 131%, reaching values of more than 10% (10.2%). This noticeable enhancement mainly attributed to the better morphology of the top deposited perovskite film (homogeneous deposition, free of pin holes, limited degradation of the perovskite by diffusion of Al atoms into the perovskite) and more efficient energy level alignment with the LUMO of perovskite the GO-Li/Ti-sol ETL induced.
E. Nouri et al.\textsuperscript{65} suggested the utilization of ultra-stable and of high performance carbon based materials instead of the organic materials PEDOT:PSS / PCBM. The authors demonstrated the use of GO in combination with NiO as HTL and Li-modified GO (GO-Li) combined with TiO\textsubscript{x} as ETL in a planar inverted PSCs (FTO/NiO/GO/Perovskite/GO-Li/TiO\textsubscript{x}/Al). Despite the lower photovoltaic performance of the GO/Li-GO cells in respect to PEDOT:PSS/PCBM devices (10.4\% over 13.1\%), the former devices exhibited much longer operational stability than the latter systems. More particularly due to the shielding against the moisture and oxygen molecules the GRM based ETL and HTL materials offer to the perovskite active layer, the GO/Li-GO PSCs retained 70\% of their initial PCE whereas the organic based cells lost more than 90\% of their initial PCE after 15 days of operation. These results encourage the use of GRM based charge transporters to prepare stable PSCs.

GQDs are nano-features with very interesting properties that have been explored in the field of organic solar cells for boosting their performance. Among these properties are the excellent electron mobilities and theirs chemical stability. J. Ryu et al.\textsuperscript{66} coated the surface of TiO\textsubscript{2} ETL of planar normal PSCs with a two nm thick film of GQDs and studied the impact of GQDs size towards the enhancement of their PCE. The optimization of the GQDs size (their LUMO is increased as theirs size is decreased and the higher efficiencies were measured for the 14 nm in diameter GQDs) maximized and accelerated (the transition time was reduced from 4.7 ns to 3.4 ns) the electron charge extraction from the MAPbI\textsubscript{3} absorber into the ETL. This approach, engineered better interface between the perovskite layer & the ETL (the roughness was reduced as the GQDs size was decreased) and resulted in an average 10\% PCE enhancement in respect to the reference device. The record acquired PCE was 19.11\%. Responsible parameters for this enhancement were (1) the lower interfacial resistance between the perovskite layer & the ETL; (2) the lower recombination rate, (3) the better induced perovskite crystallization; and (4) the proper energy alignment the 14 nm in diameter GQDs engineer between MAPbI\textsubscript{3} and TiO\textsubscript{2}, in respect to the reference devices (no use of GQDs TiO\textsubscript{2} coating). Furthermore, the exploitation of GQDs into the ETL contributed also to the reduction of current – voltage hysteresis, which can attribute to the planar structure (better balance between the hole and electron mobilities). Non-encapsulated devices that incorporated 14 nm in diameter GQDs exhibited better durability from sunlight and moisture than reference cells. This was attributed to the carbon character of the GQDs onto the TiO\textsubscript{2} layer.
ZnO has been proposed as an alternative ETL that tackles the main disadvantage of TiO\textsubscript{2} ETL (the mandatory sintering at high temperatures), since it does not request heating/sintering step to achieve the appropriate form. On top of this, ZnO demonstrates better electron mobility than TiO\textsubscript{2} and thus is suitable n-type semiconductor for PSCs. However, faces some stability issues that induce decomposition of the perovskite active layer during annealing process. The introduction of GRMs e.g. rGO within ZnO, improves even more its electron conductivity and thus help the fast charge extraction from the perovskite. Moreover the rGO passivate the ZnO and prevent the latter’s decomposition, increasing the rGO/ZnO based PSCs stability. P.S. Chandrasechar \textit{et al.}\textsuperscript{67} studied the impact of the rGO concentration (varied between 0 to 1%) on the PCE of planar normal PSCs based on rGO / ZnO ETL. Optimization of the rGO concentration into the rGO/ZnO nanocomposite (0.75%) led to the achievement of PCE higher than 10\% (10.34\%). This performance corresponds to an increase of 47\% in respect to reference PSCs based on pristine ZnO. This PCE enhancement is attributed to the superior growth of the perovskite thin-film (the crystal grain size has been increased from 10 nm to 250 nm when the perovskite deposited onto the rGO/ZnO nanocomposite in respect to ZnO ETL), the smoother morphology the perovskite film acquired (the RMS reduced from 114 nm to 61 nm) and enhanced electron transport/extraction (as confirmed from the PL signal quenching) on using the graphene network in the ETL nano-composite. Use of higher or lower rGO concentrations affected negatively the PCE of the PSCs due to graphene’s parasitic absorption (e.g. when 1\% was employed) or no uniform deposition of the perovskite film onto the ETL (e.g. when less than 0.75\% rGO was used).

Organic ETLs such as PCBM have triggered a great deal of research mainly due to their low processing temperatures, low cost fabrication. However they suffer from low electron mobilities and low conductivities. A number of metal oxide based ETLs have been proposed in various works that surmounted these obstacles, but also exhibited other disadvantages when utilized into PSCs such as hysteresis and low stability. Z. Yang \textit{et al.}\textsuperscript{68} proposed the dispersion of GQDs within PCBM ETL based normal planar MAPbI\textsubscript{3} PSCs. The inclusion of GQDs (of 5 nm in diameter) in low concentrations (0.5 wt\%) enhanced the conductivity of the PCBM and facilitated the photo-generated electrons extraction from the active layer into the ETL. Moreover and as a result of the faster extraction rate, the accumulation of charges at the interface of perovskite with the ETL was reduced and the PCE of the PSCs was increased by 20\% (from
14.68% to 17.56%). Improved stabilities under continuous solar illumination in the glove box were showed; the PCE maintained beyond 80%, with the UV component presented, after 300 hrs while the PCE of the reference cells dropped lower than 50%.

To date the primary research & commercial efforts in the field of hybrid PSCs has been focused in the enhancement of theirs PCE. However, the stability issues are still unsolved and the lack of stability protocols is a fact.\textsuperscript{69,70} In particular, the planar inverted configuration exhibits low stability issues mainly related with the easy oxidation of the low work function of metal electrodes (Al). G. H. Kim \textit{et al.}\textsuperscript{71} used fluorine functionalized graphene nano platelets (EFGnPs-F) to achieve higher stabilities in planar inverted PSCs. 82% of the initial PCE, after 30 days of exposure in ambient conditions without encapsulation, was maintained. This high stability was mainly stemmed to the super hydrophobic character (stems to the carbon-fluorine bond) and to the chemical stability of the EFGnPs-F moieties (see figure 9a-i). The latter shielded the below deposited perovskite layer, from air conditions induced degradation. More particularly when a water droplet was deposited on an EFGnPs-F layer on top of an MAPbI\textsubscript{3}/PCBM film, the contact angle was 65.5°. Furthermore, after 60s, the contact angle of EFGnPs-F remained relatively high at 58.6°. This clearly showed that the hydrophobic property of EFGnPs-F could protect the active layer from water ingress, to improve device stability. The superior stability under 50% of humidity were measured as a function of the absorption properties of the EFGnPs-F / MAPbI\textsubscript{3} films in respect to these ones of the MAPbI\textsubscript{3} reference films. Due to the low concentration of the EFGnPs-F utilized, the absorption spectrum of the EFGnPs-F / MAPbI\textsubscript{3} films did not modified from the absorption spectrum of MAPbI\textsubscript{3} film. After 10 days of storage at room temperature at 50% of humidity, was observed that the pristine MAPbI\textsubscript{3} films started to degrade (decomposition). This was confirmed from the disappearance of the characteristic IR absorption shoulder (~780 nm). In contrast this was not observed in the case of EFGnPs-F coated MAPbI\textsubscript{3} films. Even more after 30 days of storage the absorption onsets of pristine of MAPbI\textsubscript{3} and EFGnPs-F / MAPbI\textsubscript{3} films have become indistinguishable. The employment of the EFGnPs-F interlayer between the PCBM (ETL) and the metal electrode not only improved the humidity stability but also kept the photovoltaic performance unchanged to the respect of the reference devices.
In summary, the graphene based ETLs have a striking impact on the PSCs PCEs and allowed (1) the fabrication of the entire devices using temperatures no higher than 150 °C (in comparison to TiO₂ based ETLs high temperature processing) that makes PSCs as versatile in their

Figure 9. Contact angle measurements taken 5, 30, and 60 seconds after dropping water onto MAPbI₃/PCBM (a, d, and g), MAPbI₃/PCBM/EFGnPs-H (b, e, and h), and MAPbI₃/PCBM/EFGnPs-F (c, f, and i). Reproduced with permission from Ref. 70 (Copyright© 2017, American Chemical Society); (j) J-V curves of devices with G-PCBM/CQDs ETL measured under one sun illumination conditions. (k) EQE spectra. (l) Stability of encapsulated PSCs under dark and under air AM 1.5G simulated solar light. (m) Stability of encapsulated PSCs in thermal ageing test at 85 °C under 50% relative humidity. Reproduced with permission from Ref. 62 (Copyright© 2017, Nature Publishing Group); fs-TAS spectra, relative optical density as a function of wavelength, at various time delays after photoexcitation of (n) PCBM and (o) rGO:PCBM ETLs. (p) Transient band edge of bleach (symbols) and their decay fits (lines) for perovskite with rGO:PCBM (cyan) and with PCBM (green) ETLs. Reproduced with permission from Ref. 61 (Copyright© 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).
application as OPVs; (2) offered superior charge collection (due to higher conductivity and lower series resistances at the interfaces, the GRM based ETLs offer); (3) do not induce any parasitic absorption losses (as CdS does) that might lower PSCs performance; (4) do not contribute to the enhancement of the collected $J_{sc}$ due to complementary absorption spectrum to the perovskite semiconductor; (5) operate as a super-fast bridge for electron transfer from perovskite absorber to the ETL. Further modification of the rGO/mp-TiO$_2$ nanocomposite ETL with surface passivation by atomic layered deposition (ALD) could further improve the electrical properties of the composite ETL and thus boost further the PCE.

**Table 2.** Summary of the record results of graphene based ETLs in mesoporous & planar PSCs.

<table>
<thead>
<tr>
<th>Architecture / Absorber</th>
<th>ETL</th>
<th>PCE (%)</th>
<th>Other Benefits</th>
<th>ΔPCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoscopic / CH$_3$NH$_3$PbI$_3$ Cl$_x$</td>
<td>LPE Graphene Nanoflakes / bl - TiO$_2$ NPs composite</td>
<td>15.6</td>
<td>Low cost fabrication (Low temperature processing)</td>
<td>53 (TiO$_2$)</td>
<td>J.T.W. Wang et al. 2014 [48]</td>
</tr>
<tr>
<td>Mesoscopic / CH$_3$NH$_3$PbI$_3$</td>
<td>GQDs as an interlayer between the perovskite and the mp TiO$_2$</td>
<td>10.15</td>
<td>N/A</td>
<td>15 (no use of GODs)</td>
<td>Z. Zhu et al. 2014 [49]</td>
</tr>
<tr>
<td>Mesoscopic / CH$_3$NH$_3$PbI$_3$</td>
<td>Graphene / mp-SrTiO$_3$ nanocomposite</td>
<td>10</td>
<td>N/A</td>
<td>46 (mp-SrTiO$_3$)</td>
<td>C. Wang et al. 2015 [52]</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI$_3$</td>
<td>rGO in mp-TiO$_2$</td>
<td>14.5</td>
<td>N/A</td>
<td>18 (mp-TiO$_2$)</td>
<td>G.S. Han et al. 2015 [53]</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI$_3$</td>
<td>rGO in bl-TiO$_2$ and mp – TiO$_2$ layers</td>
<td>9.29</td>
<td>N/A</td>
<td>40 (free of rGO)</td>
<td>T. Umeyama et al. 2015 [54]</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI$_3$</td>
<td>mp-GP-Cs$_2$CO$_3$</td>
<td>13.8</td>
<td>Thermal Stability</td>
<td>48 (rGO-Cs$_2$CO$_3$)</td>
<td>S. W. Tong et al. 2016 [56]</td>
</tr>
<tr>
<td>Structure Type / Material</td>
<td>Interlayer / scaffold</td>
<td>Stability</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
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</tr>
<tr>
<td>Mesoscopic / MAPbI₃</td>
<td>ZSO/rGO</td>
<td>8.53</td>
<td>S. S. Mali et al. 2016 [57]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoscopic / MAPbI₃</td>
<td>rGO - mp-TiO₂</td>
<td>19.54</td>
<td>K. T. Cho et al. 2016 [58]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoscopic / MAPbI₃</td>
<td>Graphene – mp-TiO₂</td>
<td>14.6</td>
<td>A. Agresti et al. 2016 [59]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesoscopic Module / MAPbI₃</td>
<td>Graphene flakes into mp-TiO₂ &amp; GO-Li interlayer</td>
<td>12.6</td>
<td>A. Agresti et al. 2017 [60]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar normal / MAPbI₃</td>
<td>Reduced Graphene Scaffold (rGS)</td>
<td>17.2</td>
<td>M.M. Tavakoli et al. 2016 [61]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃₋ₓClₓ</td>
<td>rGO - PCBM</td>
<td>13.5</td>
<td>G. Kakavelakis et al. 2017 [62]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>CQDs/G-PCBM</td>
<td>17.0</td>
<td>E. Bi et al. 2017 [63]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>GO-Li/Ti sol</td>
<td>10.2</td>
<td>E. Nouri et al. 2017 [64]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>PCBM / TiO₂ / GO-Li</td>
<td>10.4</td>
<td>E. Nouri et al. 2018 [65]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Normal / MAPbI₃</td>
<td>GQDs into cp-TiO₂</td>
<td>19.11</td>
<td>J. Ryu et al. 2017 [66]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Normal / MAPbI₃</td>
<td>rGO/ZnO composite</td>
<td>10.34</td>
<td>P.S. Chandrasechar et al. 2017 [67]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Planar Normal / MAPbI₃</td>
<td>PCBM/GQDs</td>
<td>17.56</td>
<td>Z. Yang et al. 2017 [68]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A large amount of energy is lost in PSCs at the interfaces of perovskite absorber with the interlayers due to charge recombination. The latter is resulting from the imperfect crystallization passivation and interfacial behavior. Moreover the enhancement of the long-term stability of PSCs is one of the most important challenges for their commercialization. The GRMs have started to be investigated quiet intensively as efficient and stable under ambient & illumination conditions HTL materials in PSCs. Table 3 summarizes the record results that have been reported in the literature regarding the utilization of GRMs into the HTL or as an interlayer between the perovskite and the HTL in mesoporous and planar PSCs.

**Mesoscopic PSCs**

J. Cao et al. used thiolated nanographene pethiolated tri-sulfur-annulated hexa-peri-hexabenzocoronene (TSHBC) as the HTM in mesoscopic MAPbI$_3$ based PSCs. The employment of nanographene provided a lot of flexibility regarding their physical and chemical nature that is defined by their size. In general nanographene (nano-size graphene flakes) are typical p – type semiconductors that its energy levels can be tuned easily through functionalization. This renders nanographene as one of the most promising candidates for HTMs in PSCs. The utilization of nanographene – TSHBC nanocomposite in PSCs (thickness of the order of 20 nm, with the optimized ratio of TSHBC/graphene to be 5:1 weight ratio) as HTM, enhanced their efficiency, mainly due to rapid hole extraction through the TSHBC, their fast transportation to the respective electrode and their long term stability due to the hydrophobic nature of nanographene. This resulted in PCEs of 14% which corresponded to ~ 15% PCE enhancement in respect to bare TSHBC HTM based PSCs. More over the non-encapsulated TSHBC/graphene based devices retained more than 95% of its operational stability, under 45% humidity, for 10 days. On the other hand the spiro – OMeTAD based PSCs performance was decreased to 25% of its initial value within 60 minutes under illumination conditions at AM 1.5 G.
W. Li et al.\textsuperscript{73} demonstrated the importance of the interface quality between perovskite and HTL (Spiro MeOTAD) for the PCE of mesoscopic PSCs. This interface quality is mainly defined by how wide and homogeneously the HTL has been deposited onto the perovskite film surface. The most commonly used surfactant that assists the reduction of the contact angle (CA) between the HTL and the perovskite is the TBP. It has been reported that introduction of TBP into HTL causes perovskite fading and corrosion. Motivated by the need of higher quality interfaces that will generate higher $J_{sc}$, FF and $V_{oc}$, the authors proposed a GO based interlayer as an alternative surfactant to improve the interface between the perovskite and the HTL. The impact of the proposed GO interlayer was impressive since (1) decreased the contact angle between the HTL and the perovskite layer (zero degrees from 13.4\textdegree); and (2) functioned as electron blocking layer (it is an insulator) reducing the recombination rate in the employed device. As a result the performance of the GO based PSC was improved by 45.5\%, mainly due to the enhancement of the short circuit current $J_{sc}$ & FF acquired values, providing PSCs with demonstrated PCEs up to 14.5\% (record value 15.1\%). The record results were obtained for an optimized GO concentration that was 85 mg L\textsuperscript{-1} (enough for GO to cover the perovskite film as a buffer layer).

The most popular used solid state HTL in PSCs is the p-type organic small molecule spiro-OMeTAD. Due to its nitrogen sp\textsuperscript{3} hybridization, large intermolecular distances are formed, which result in poor conductivities. This is detrimental to the performance of the PSCs. Intense research effort has spent in order to dope the existed p-type materials (e.g. use of Li-TFSI) or to improve the contact between perovskite and HTM (e.g. use of pyridine derivatives). Although these methods improved the HTL conductivity, introduced either perovskite absorber degradation (due to hydroscopic character of Li TFSI) or were corrosive to the perovskite (pyridine derivatives). These side effects are harmful to the device stability and new strategies should be employed to introduce new HTL with higher demonstrated conductance and without the use of Li-TFSI and pyridine dopants. Q. Luo et al.\textsuperscript{74} proposed the employment of RGO as a stable conductive additive combined with dopant free spiro-OMeTAD as an efficient HTM in PSCs. The use of the proposed bilayer led to PCE up to 10.6\%, which were more than 70\% higher than the dopant free spiro-OMeTAD HTL based cells. Moreover the stability of the bilayer based HTL device was superior than this one of dopant free spiro-OMeTAD cells; the bilayer device remained over 85\% of its PCE initial value after 500 hrs in air & under dark
conditions (the corresponding stability of the dopant free spiro–OMeTAD cells decreased to 35% of its PCE within the same time). This enhanced stability was attributed to the absence of either Li-TSFI or corrosive pyridine additives. The enhanced performance of the bilayer based on cells were attributed to (1) the higher conductivity the rGO layer added to the HTL material; rGO conductivity apart of the reduction process was further enhanced due to its iodine ((p-dopant)) doping during the reduction (rGO conductivities as high as 2600 Sm⁻¹ were measured); (2) the high hole quenching ability the bilayer rGO/dopant free spiroOMeTAD HTL bilayer provided when interfaced with the perovskite active layer (MAPbI₃); (3) the rGO layer provided better interfaces between the perovskite layer & the HTL and thus better charge extraction; (4) the introduction of three interfaces through which the holes can be extracted and be collected in the metallic back electrode: perovskite/rGO, perovskite/dopant free spiro OMeTAD and through spiro OMeTAD / rGO interface.

Despite Spiro-OMeTAD advantages (solution processed, tunability of its energy levels, good energy matching with the most common used perovskite semiconductors) compared to other inorganic and organic employed HTMs, it suffers from specific drawbacks such as high cost, low hole mobility, low demonstrated stability when its doped version is utilized in complete cells. All these drawbacks oblige the scientific community to search for new potential candidates as low cost, chemical doping free, HTLs for long term stable PSCs. A.L. Palma et al.⁷⁵ addressed the Spiro – OMeTAD challenges using rGO as HTL in mesoscopic PSC. The built rGO based devices, demonstrated superior long-term stability compared to the doped Spiro – OMeTAD reference cells. More specifically, the as prepared rGO cells after 1987 h of shelf life test, exhibited an increase of their PCE by more than 30% (from 4.9% to 6.6%) whereas the Spiro-OMeTAD cells PCE degraded from its initial value of 11.1 % to 6.5%. The stability of all the devices tested under the ISOS-D-1 self-life ageing protocol for 138 hrs (unsealed cells in air, in dark, at ambient temperature, and R.H. (50%)). The endurance tests showed the degradation of the reference devices PCE by 56%. Contrary the rGO spray coated PSCs demonstrated superior stability behavior. The rGO and the reference cells were also tested under the ISOS-L-2 stress protocol under light soaking at 65 °C. In this case, during the 1st 138 h, the reference device PCEs dropped over 55% where the rGO based PSCs lost less than 11%. Moreover, under the 1987 total stress time & under light soaking, the rGO cells showed an enhancement of their PCE from 4.9% to 6.6% which was higher than this one exhibited by the reference devices after the
same test period (PCE ~ 6.6%). The increase of the rGO based cells under light soaking was attributed to the passivation of the charge traps. In the case of the Spiro – OMeTAD cells the degradation induced by the additives has stronger impact on the final performance of the PSC. These results clearly indicate the better lifetime of the rGO-based PSC with respect to the Spiro – OMeTAD based devices. The authors linked the long term stability of the rGO based cells to the following parameters: (1) GO reduction method employed; (2) rGO solvent physico – chemical properties (that might corrode the perovskite layer); (3) rGO deposition technique (spay coating was preferred than spin coating); (4) rGO HTL are free of additives, necessary for the doping of the Spiro – OMeTAD and led to cells degradation.

Many of the instabilities issues in mesoscopic PSCs, originate from the organic transport layers sensitivity in atmospheric conditions (moisture and oxygen). F. Wang et al.\textsuperscript{76} suggested the utilization of a combination of single-walled carbon nanotubes / graphene oxide (SWNT/GO) as an efficient & stable HTL/electron blocking layer in glass/FTO/c-TiO2/mp-TiO2/MAPbI\textsubscript{3}/HTL/PMMA/Au PSCs. The combination of (SWNT/GO) resulted in a high conductive (due to the presence of the SWNT), less hysteresis, fast hole transportation, efficient electron blocking (due to the presence of the GO that resulted in lower charge recombination rates due to better energy level alignment between the perovskite layer and the HTL that led to PCEs of 13.3 %. This performance represented a PCE enhancement compared to the free HTL based reference device of the order of 303%. The deposition, through spin coated, of the PMAA (thickness of 100 nm) on top of the SWNT / GO HTL, resulted in a substantial increase of the device lifetime in air (humidity: 70 – 80%, at room temperature). More particularly, the PCE of the perovskite / spiro – OMeTAD based devices was dropped under the aforementioned conditions from 10.5% to 5.8% within ten days. In contrast, the SWNT/GO/PMMA cells maintained almost unaffected theirs PCE; from 10.5% modified by 5% to 10.0%.

P3HT doped with TBP and Li-TSFI has recently been proposed as an inexpensive HTL utilized in PSCs alternative to the SpiroOMeTAD. However, doped P3HT contributes to lower PCEs in respect to the doped SpiroOMeTAD based devices. Moreover and in comparison to SpiroOMeTAD operates as a shield for the perovskite active layer by protecting it against the moisture and thus fast degradation. At the same time GRM based HTLs in PSCs have a dual beneficial role that of the PCE and the thermal stability enhancer. T. Gatti et al.\textsuperscript{77} proposed the
utilization of chemically functionalized rGO with p-methoxyphenyl (PhOMe) dispersed into the P3HT matrix in solution. The chemical functionalization of the rGO with PhOMe is dictated in order the rGO do not be aggregated and to be uniformly & stably dispersed within the polymer matrix. The record results were achieved for an optimum rGO – PhOMe concentration within the polymer matrix (4%) above which the aggregation of the rGO caused the lower performance of the overall device. Mainly due to hole transfer facilitation from the perovskite layer into the HTL, the PCE of the rGO-PhOMe/P3HT HTL based MAPbI$_3$ mesoscopic devices increased by more than 15% (PCE increased from 6.5% to almost 10%) in respect to the reference bare P3HT HTL based PSCs. Moreover the exploitation of the rGO-PhOMe/P3HT HTL in PSCs is beneficial for their stability, since slowed down the device degradation due to its exposure to environmental factors such as moisture or oxygen. Endurance tests carried out for 3240 hrs in dark, have shown that average PCE of the graphene based HTL cells of 4.7% have recorded. In comparison the bare P3HT HTL based cells have exhibited PCEs, for the same test period, almost equal to zero. This improvement was attributed to the fact that rGO – PhOMe provided a more hydrophobic protective layer with the respect of the pristine polymer.

J. Ye et al.$^{78}$ based on the advantages of P3HT over spiro – OMeTAD (low cost, easier processing) and motivated by its disadvantages (low hole mobility), proposed the composite of P3HT:F-Graphene (Functional Graphene) (4% of Graphene) as a high performed HTL in mesoporous PSCs. The P3HT:F-Graphene based PSCs demonstrated 18% higher PCE (8.05% vs 13.57%) and superior stability (35% vs 70% of the pristine PCE) under storage in ambient atmosphere (25 °C, humidity 20 – 40 %) for eight weeks in respect to P3HT based devices. This prolonged stability under moisture exposure is attributed to the hydrophobicity of the graphene. Moreover thanks to the higher hole conductivity and better energy level alignment between the VB of P3HT and the VB of the MAPbI$_3$, due to the presence of the F-Graphene to an optimum concentration (4%), more efficient charge extraction occurred from the MAPbI$_3$ into the HTL.

In pursuit of higher efficiencies in PSCs technology, the scientists should deal with a deficiency that characterize all the ionic crystals: the defects in their surface and the grain boundaries due to the under coordinated I, Pb$^{+2}$, ions. The latter operate as recombination centers for the photo-generated carriers and thus limit the maximum PCE can be obtained. X. Wen et al.$^{79}$ proposed a passivation technique that involving balancing the under coordinated Pb$^+$
ions with molecules of the opposite charge. More particularly, they showed that the incorporation of amino functionalized rGO (NGs) as an interlayer between the MAPbI$_3$ absorber and the spiro – OMeTAD HTL, can passivate the under coordinated Pb$^{+2}$. As a result of the passivation effect by the amino group (the N atoms interact with the under coordinated Pb$^{+2}$ atoms) and the high hole mobilities of the rGO, mesoscopic NG based PSCs exhibited higher photovoltaic performance ($\Delta$PCE: 36%) compared to the reference (no use of NGs interlayer) devices. The PCE advancement, from 10.7% to 14.6%, has been attributed mainly to $J_{sc}$ & FF enhancements. Moreover EIS and PL measurements indicated the lower recombination rates and the better hole extraction kinetics for the NGs based cells on agreement with the superior photovoltaic performance.

One of the most recently proposed HTL materials, that tackles the Spiro-OMeTAD obstacles, is the solution processed copper phthalocyanine (CuBuPc). CuBuPc based PSCs did not exhibited higher photovoltaic performances but demonstrated higher stability and are of lower commercial price in respect to the spiro-OMeTAD cells. E. Nouri et al. studied the exploitation of CuBuPc and GO as HTL/buffer-layer system applied in mesoscopic PSCs. This PSC showed enhanced PCEs in respect to the reference device (7.3 %, spiro-OMeTAD) of the order of 14.4%. This enhancement is mainly attributed to the higher values of the $V_{oc}$ and FF, which higher values were a clear indication of blocking (the presence of the buffer layer) the shunt paths (due to aggregation of CuBuPc) across the cell. EIS and PL measurements showed that the GO buffer layer facilitated also the transportation of photo-generated holes from the perovskite into the HTL and thus reducing the charge carrier recombination. The stability of the device also improved due to the hydrophobicity and water repelling capacity of GO.

The building of PSCs with efficiencies higher than 20% using inorganic, thermal & chemical stable, low cost HTL materials remains a key goal to foster the large scale deployment of this 3rd generation solar cell technology. Among the proposals have been published, the choice of CuSCN looks one of the most promising since this material is accompanied by very attractive features such as (1) low cost; (2) p-type conductivity; (3) well aligned VB with the majority of perovskite semiconductors employed nowadays in solar cells. However a critical issue associated with the exploitation of this material is that its solvents degrade fast the perovskite layer. This issue has been moderate tackled using inverted device architecture. N. Arora et al. used the
mesoscopic TiO$_2$ based normal device architecture and drop casted uniformly a thin and free of pin holes CuSCN layer (thickness of ~ 60 nm) that fully covered the below CsFAMAPbI$_{3-x}$Br$_x$ perovskite layer without degrading the latter’s quality (because of the dynamic, than the conventional, deposition approach selected). Initially the thin layer of CuSCN was positioned between the perovskite and the gold electrode. The high hole extraction rates achieved using the CuSCN HTL in respect to HTL free perovskite cells, was revealed by the PL quenching in the case of CuSCN based PSCs. Moreover time correlated single photon counting (TCSPC) spectroscopy allowed the calculation of the dynamics of charge carriers. In agreement with the steady state PL, the hole transfer was faster across the perovskite – CuSCN interface as compared to the perovskite – spiro OMeTAD junction. The device with CuSCN HTL and the rGO as an interlayer yielded a $J_{sc}$ of 23.24 mA/cm$^2$, $V_{oc}$ = 1.11 V and a FF of 0.78. These photovoltaic figures resulted in PCEs of 20.4% (see Figures 10 a-e). The long term thermal stability at high temperatures is an imperative feature. The CuSCN based devices showed poor photo-stability, losing > 50% of their initial PCE merely within 24 hours, due to an electrical reaction between the gold with the thiocyanate anions forming an undesired barrier. The incorporation of the rGO interlayer between the CuSCN and the gold electrodes improved substantially the photo-stability of the PSCs. The resulting PSCs retained > 95% of their initial efficiency after aging 1000 hrs (see Figure 10 f).
Figure 10. J-V curve of the (a) spiro-OMeTAD and (b) CuSCN-based PSCs (both insets shows the V_{oc} as a function of illumination intensity and the ideality factor for each case). (c) PV characteristics with standard deviations for both spiro-OMeTAD and CuSCN based PSCs. (d) MPPT for 60 s, yielding stabilized efficiencies of 20.5% and 20.2%, respectively, for spiro-OMeTAD–based and CuSCN-based PSCs. (e) EQE spectra recorded for both spiro-
OMeTAD–based and CuSCN-based PSCs. (f) Long-term lifetime of an unsealed CuSCN-based PSC with and without a thin layer of rGO (as a spacer layer between CuSCN and Au electrode), monitored at MPPT under continuous full-sun illumination at 60°C in a nitrogen atmosphere. Reproduced with permission from Ref. 80 (Copyright© 2017, American Association for the Advancement of Science).

Planar PSCs

GRMs tackle some of the PEDOT:PSS, the most commonly used HTL material, problematic characteristics such as hydrophilicity that permits the infiltration of water into the cells active layer and thus the photovoltaic performance degradation of the cell. J. Kim et al.\textsuperscript{82} proposed the
use of solution processed nitrogen doped graphene oxide nanoribbons (NGONRs) as an alternative to PEDOT:PSS as an HTL in planar inverted PSCs (FTO/NGONR/MAPbI₃/ZnO NPs/Al). The NGONRs based cells demonstrated 19% higher PCE compared to the PEDOT:PSS cells (from 10.86 to 12.94 %). This higher efficiency was attributed to the higher acquired J_{sc}, V_{oc} values and to the higher transparency of the NGONRs compared to the PEDOT:PSS devices. The impact of the NGONRs utilization was multiple since it was responsible for the better & more homogeneously MAPbI₃ film, better energy level matching with the VB & the CB of MAPbI₃ semiconductor (the NGONRs energy level tuning is controlled by the doping level), the efficient & fast transportation of holes from the active layer to the HTL (the average PL decay rate has been reduced from 83 ns to 22 ns), the low demonstrated hysteresis and the extension of the cells’ stability under room temperature & humidity conditions.

Z. Wu et al. investigated the application of GO as HTL in planar inverted PSCs and studied its impact into the various photovoltaic characteristics of PSCs when replaced PEDOT:PSS in terms of performance and stability. GO was utilized as HTL in mixed halide perovskite solar cells due to its ideal characteristic: (1) suitable work function (~4.9 eV) that formulates ideal energy level alignment with the energy levels of the mixed halide perovskite semiconductor; (2) acceptable vertical resistivity; (3) its surface doping effect on the active layer. All these GO characteristics facilitated the superior charge transfer and charge collection in the PSCs (ITO/GO/CH₃NH₃PbI₃-xClₓ/PCBM/ZnO/Al) incorporated the graphene based HTLs compared to the PEDOT:PSS reference devices. The authors showed that the thickness of the spin coated GO onto ITO, strongly affected the charge transfer (as this process is revealed from PL measurements) from the active layer into the HTL. Theirs study concluded that the thicker the GO HTL (2 nm, 6 nm and 20 nm thick HTLs were tested) was, the stronger the steady PL quenching was observed. The 2 nm thick GO displayed similar quenching with the TiO₂ (~ 48%) whereas a 20 nm thick GO displayed a slightly superior quenching (~ 98%) than PEDOT:PSS based cells. The higher charge extraction between GO and perovskite, when thicker GO HTL was undertaken, was attributed to the larger coverage ratio and higher roughness between perovskite and GO. Motivated by the high charge extraction demonstrated between GO and perovskite semiconductor, a number of complete PSCs were fabricated. The record results were acquired for the cell employed the thinnest GO layer (~ 2nm thickness). The PCE has been enhanced (from 9.26% to 12.4%) by almost 20% compared to the control device based on
PEDOT:PSS HTL. Despite the higher quenching the thicker GO lowered the absorption of the active layer and thus reduced the device PCE. Moreover the thicker the GO layer, increased the demonstrated series resistance of the device. The superior performance of the cells incorporated ultrathin GO HTL was also attributed to the more balanced charge mobilities provided between electrons and holes (compared to the PEDOT:PSS devices) that prohibited the charge accumulation and contributed to the enhancement of the device PCE (higher FFs). GO also facilitated the fast growth, of large grain domain size and of higher orientation order, perovskite crystals (of micron sized) that also contributed to the received very promising reported results. The less porosity the perovskite film demonstrated when spin coated onto GO HTL instead of PEDOT:PSS was the primary reason for the lower dark currents the GO devices exhibited and the superior performance compared to the PEDOT:PSS. Also the higher roughness the perovskite film demonstrated onto GO compared to the PEDOT:PSS HTL deposition layer, provided a more efficient light trapping when employed as an active layer into complete device.

Unlike the intense research implemented to find new ETL materials with superior properties (conductivity, rapid electron transportation from the perovskite layer, easy deposition techniques, low temperature processing, thickness controllability) to be employed into the PSCs, less effort has been undertaken for new innovative HTL materials. The most popular used HTL is the PEDOT:PSS that is accompanied with well known disadvantages: hygroscopicity and acidity. These disadvantages are detrimental for the long-term stability exhibited by the corresponding PSC devices. Other alternative HTL materials were proposed (e.g. nickel oxides, GO) but either demonstrated high temperature processing that nullify the solution processing. J. S. Yeo et al.\textsuperscript{84} presented the application of solution-processed rGO as an ultrathin (3 nm) HTL in planar PSCs employed MAPbI\textsubscript{3} as an absorber. rGO demonstrated all the characteristics of an ideal HTL: low temperature processing, conductivity, abundance, stability and higher work function than conventional PEDOT:PSS. The PSCs employed rGO HTLs exhibited higher PCE (PCE ~ 10.8%, Voc = 0.95 V, Jsc = 14.81 mA/cm\textsuperscript{2}, FF = 71.13%) and superior stability than similar reference devices employing PEDOT:PSS (PCE ~ 9.14%, Voc = 0.92 V, Jsc = 13.65 mA/cm\textsuperscript{2}, FF = 69.97%) or GO (PCE ~ 4.04 %, Voc = 0.89 V, Jsc = 10.70 mA/cm\textsuperscript{2}, FF = 37.61 %) as HTL. The better energy level matching between the rGO and the MAPbI\textsubscript{3} compared to that between PEDOT:PSS and MAPbI\textsubscript{3} was one of the facts that attributed the better observed PCE. This more suitable energy level matching generated fewer losses and facilitated the charge
transfer across the interface of perovskite layer/HTL generating higher PCEs. The steady state PL quenching was also a figure of merit to demonstrate the better charge transfer from the MAPbI$_3$ absorber through the selected HTL; the higher quenching was reported when rGO picked up as HTL. Time resolved photoluminescence (TRPL) measurements also suggested that when rGO was employed led to faster charge extraction and reduced recombination compared to the PEDOT:PSS case. The superiority to convert the incoming photons to current of the rGO compared to the PEDOT:PSS cells was revealed by the higher EQE & IQE curves the former characterized. To further unveil the impact of rGO on the MAPbI$_3$ morphology, the SEM images showed that longer perovskite grain sizes were obtained, 100 – 200 nm compared to below 100 nm achieved with the PEDOT:PSS. Also the XRD spectra revealed better crystallinity of the MAPbI$_3$ when processed onto rGO instead of PEDOT:PSS (narrower FWHM of the 110 XRD peak). To further emphasize the beneficial role of selecting rGO compared to PEDOT:PSS the PSCs were evaluated regarding their stability under ambient operational conditions. The rGO based PSCs remained the 62% of their initial PCE even after 140 hrs of continuous illumination whereas the PEDOT:PSS cells have fully degraded within this duration. The reasoning is the shielding the rGO provided to the perovskite absorber against the oxygen and moisture due to its passivation ability against these elements.

It has been noticed recently an increased research activity to demonstrate the prospects of flexible perovskite solar cells. On the frame of this effort, the researchers are looking for new, low temperature (below 120 °C), solution processed materials to be employed as HTL, ETL, electrodes and deposition substrates in flexible PSC. Until recently the main drawback in these efforts was the poor performance of these flexible cells mainly due to charge recombination and structural or chemical defects in the perovskite films. T. Liu et al.\cite{85} exploiting (1) the exceptional electronic, optical, thermal and mechanical properties of graphene oxide (GO); (2) the facile way to tune GO WF using silver trifluoromethanesulfonate (AgOTf) dopants and achieve GO p-doping, managed to report the application of a new composite low temperature processed HTL, PEDOT:PSS:AgOTf-doped GO, in flexible PSCs. The dopants concentration in GO fully controlled the electrical ($R_s$, conductivity), physical (WF, transmittance), morphological (roughness, thickness) of the low temperature processed HTL. The incorporation of PEDOT:PSS:AgOTf-doped GO HTL permitted the entire device to be prepared at temperatures less than 120 °C. The build devices, deposited on rigid (glass/ITO) or in flexible substrates
(PET/ITO or PET/AZO/Ag/AZO) exhibited competitive PCEs: 11.9%, 9.67% and 7.97% respectively. The high performance of the PEDOT:PSS:AgOTf-doped GO based PSCs was attributed to (1) the better energy level alignment between the HTL (WF~ - 4.6 eV) and the perovskite absorber (CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$, VB~ -5.3 eV) that permitted the easiest hole transportation and the higher electron blocking; (2) the lower $R_s$ the HTL demonstrated (compared to the PEDOT:PSS) due to GO p-doping: from 228 Ω sq$^{-1}$ (before the GO doping) was reduced to 118 Ω sq$^{-1}$ upon the GO doping. This lowering of the $R_s$ facilitated the faster transportation of holes through the HTL, the lower charge recombination and thus the more efficient charge collection. Regarding the flexibility properties of the build ITO free PSCs, and especially the device on PET/AZO/Ag/AZO, demonstrated exceptional mechanical properties: the PCE degraded by only 1.26% after 2000 bending cycles. This small degradation in the PCE was mainly due to reduced FF.

Pristine PEDOT:PSS suffers from micromorphology inhomogenieties, chemical instabilities issues and demonstrates electrical conductivity gradients as moving from the exterior into the interior. All these issues should be tackled since PEDOT:PSS is one of the most used HTL in the planar inverted architecture of PSCs. X. Huang et al.\cite{86} proposed the immersion of thermally reduced single layer of rGO into the PEDOT:PSS. The employment of the proposed composite led to devices, based on MAPbI$_3$ absorber, with 22.1% superior PCE compared to the reference PEDOT:PSS planar inverted PSCs. The performance of the rGO/PEDOT:PSS HTL devices was optimized as a function of the rGO concentration used into the HTL. The record results were obtained when 1:1 v/v rGO to PEDOT:PSS was dispersed; whereas the PCE was jumped from 8.7 to 10.6%. The higher PCEs were attributed to the lower dark currents and higher shunt resistance of the rGO/PEDOT:PSS based devices. These improved electrical characteristics increased the obtained $V_{oc}$ and FF values compared to the respective ones of the reference device. According to the UV/visible absorption, AFM and XRD measurements, the addition of the rGO did not impact the transmission, the roughness and the crystallization of the ITO/PEDOT:PSS and MAPbI$_3$ respectively.

The planar PSCs architecture is free of the complexities of the mesoporous design as for example the high processing temperatures requested for the crystallization of the TiO$_2$ or the low temperature instabilities of the Al$_2$O$_3$ scaffolds. One strategy to improve the planar PSCs PCE is the engineering of the electronic, morphological and stability properties of the charge transfer
layers. To tackle this issue, the engineering of innovative interlayers is an intelligent solution towards high efficiency PSCs. Even the incorporation of GO films as an interlayer, between the perovskite absorber and the HTL, have contributed to the enhancement of the planar architecture’s PCE, the difficulties to homogeneously deposit them onto the ITO should be overcomed. S. Feng et al.\textsuperscript{87} demonstrated the introduction of an spin coated ammonia modified graphene oxide (GO:NH$_3$) interlayer between HTL (PEDOT:PSS) and the CH$_3$NH$_3$PbI$_3$-xCl$_x$ in a planar inverted PSC. The incorporation of the GO:NH$_3$ interlayer (the record results were taken for the GO:NH$_3$ ratio 1:0.3) assisted the PCE enhancement compared to the reference device (without GO:NH$_3$) to be increased from 12.11\% to 16.1\%. The author’s proposal combined the high conductivity of the PEDOT:PSS & GO and the stability against the moisture the GO:NH$_3$ offers. The exhibited PCE improvement by 33\% (all the photovoltaic parameters increased) was partially attributed to the improved crystallization (longer grain size) & preferred in plane orientation of the perovskite crystals, partially to the nearly coverage of PEDOT:PSS, partially to the improved absorption (in the range between 360 and 640 nm) due to the inclusion of the GO:NH$_3$, partially to the improved stability under ambient conditions (after 96 hrs of testing the PEDOT:PSS - GO:NH$_3$ cell PCE was degraded by 28\% whereas the PEDOT:PSS control device PCE reduced to 65.6\% of its initial value) and finally partially to the better energy alignment between the PEDOT:PSS and CH$_3$NH$_3$PbI$_3$-xCl$_x$ (the WF of the PEDOT:PSS-GO:NH$_3$ has been increased from 5.1 to 5.37 eV, due to the N adsorption onto the GO, and the VB of the perovskite absorber is measured at 5.4 eV). The GO-NH$_3$ based devices exhibited the smallest hysteresis behavior than the control devices. This was related to the improved perovksite crystallization and preferred orientation, to morphological changes and better energy alignment at the perovskite interface.

Despite the impressive physical, electronic properties and the demonstrated PCEs of PSCs, there are still some issues, mainly related to the stability that hold their commercialization. Scientific reports and publications revealed that interface quality between the perovskite layer and the transport layers can define the stability and performance of these very promising solar cells. A. Giuri et al.\textsuperscript{88} proposed an alternative HTL made by a nanocomposite of PEDOT:PSS and UV reduced GO. The proposed buffer layer employed in planar inverted MAPbI$_3$ PSCs and was responsible for the higher improvement in PCE by 240\%; the PCE has been increased from 2.17\% to 7.39\%. Moreover the thermal stability of the HTL for temperatures above 250°C, the
wettability of perovskite precursor onto the PEDOT:PSS/rGO HTL, the morphology of MAPbI₃, the charge transfer through the interface of perovskite layer & HTL, have been improved compared to the PEDOT:PSS respective devices. The PCE enhancement, was attributed to these improvements and is reflected in higher acquired V_{oc} and FF values compared to the PEDOT:PSS cells. The only PV parameter that reduced was was the J_{sc} due to the higher R_{s} the PEDOT:PSS/rGO HTL demonstrated compared to the PEDOT:PSS films.; after the immersion of the GO the R_{s} of the PEDOT:PSS increased from 100 Ω/sq to 5kΩ/sq. However this ‘side’ effect did not stopped the enhancement of the overall PCE of the PEDOT:PSS/rGO cells.

D. Y. Lee et al.⁸⁹ proposed the utilization of a composite of GO/PEDOT:PSS as HTL in planar inverted PSCs. The suggested composite can complement the drawbacks of a single GO and conventional PEDOT:PSS. The GO/PEDOT:PSS HTL based MAPbI₃ PSCs demonstrated higher EQE in respect to the PEDOT:PSS based MAPbI₃ cells. This enhancement was attributed to several parameters such as (1) the better alignment of energy levels between the energy levels of the HTL and the perovskite active layer that also secured superior electron blocking capabilities; (2) to the planarization & pin hole free HTLs; (3) to the lower and higher sheet and shunt resistance respectively. As a result the PCE of the GO/PEDOT:PSS HTL based MAPbI₃ cells was increased by 18.34% (from 8.23% to 9.74%), mainly due to the enhancement of the J_{sc}. Moreover the inclusion of the GO into the HTL prohibits the diffusion of ITO with highly acidic PEDOT:PSS. As a result, the under atmospheric conditions operation (temperature of 21 – 24 °C and humidity of 38 – 55%) demonstrated stability of the GO/PEDOT:PSS based PSCs was further increased in respect to the PEDOT:PSS based cells.

PEDOT:PSS due to its good film forming property, excellent transparency in the visible and near infrared regions and good conductivity is the main HTL material used in planar inverted PSCs. PEDOT:PSS is well studied for its drawbacks when employed in PSCs, such as its acidic character and inefficient electron blocking capability. There are reports that introduce new materials (such as V₂O₅, NiOₓ, CuSCN) to replace PEDOT:PSS, free of its disadvantages. Other publications propose another alternative which is the use of PEDOT:PSS as a composite HTL material in combination with innovative materials such as GRMs. D. Li et al.⁹⁰ studied the performance of GO / PEDOT:PSS hybrid bilayer as a HTL for MAPbI₃ based planar inverted PSCs. The GO modification strategy takes advantages of high conductivity of PEDOT:PSS and the GO electron-blocking (due to its high LUMO level, -1.6 eV, compared to the CB of MAPbI₃
-3.9 eV) and hole transfer facilitator capabilities. The suppression of the leakage current, the reduced recombination rate, due to the improved hole extraction, the higher absorption at around 750 – 790 nm, the better MAPbI$_3$ morphology, resulted in 30% improvement of the PCE (from 10% to 13.1%) compared to the control device. One of the main findings of this research was that as the GO thickness increased the solar cell PCE decreased. This was attributed to the less transparency and conductivity the thicker GO layers resulted. The record PCE results were obtained for an ultrathin film of GO (~ 2 nm). The major contribution to the enhancement of PCE lies on the increased $V_{oc}$ and FF values in respect to the reference device.

The GRMs have started to be investigated quiet intensively as efficient and stable under ambient & illumination conditions HTLs in PSCs. More particularly, GRMs tackle some of the most commonly used HTLs issues such as hydrophilicity that permits the infiltration of water into the devices perovskite active layer and thus the fast degradation of the PSCs. H. Chen et al.\textsuperscript{91} underpinned that the water diffusion into PSCs can be faced using advanced interface engineering. The authors proposed the use of solution processed oxo – functionalized graphene (oxo – G$_1$) instead of the hydrophilic PEDOT:PSS as a HTL for PSCs. The resulting planar inverted PSCs exhibited PCEs of up to 15.2% and enhanced operational lifetime under dark and light soaking conditions. Not sealed PSCs retain 80% of their initial PCE after 500 hrs of white light illumination and approximately 60% of the initial PCE after ~ 1000 hrs under ambient conditions. On the contrary, PEDOT:PSS cells retained only the 5% of their initial PCE after 50 hrs of white illumination. Additionally, the oxo-G$_1$ HTL based PSCs kept 92% of their initial PCE after 1900 hrs dark storage conditions in ambient conditions. The superior lifetime of the oxo – G$_1$ HTL based PSCs as compared to PEDOT:PSS PSCs, was attributed to its hydrophobic character and potential better moisture barrier properties of oxo-G$_1$.

A. Giuri et al.\textsuperscript{92} demonstrated the synergetic beneficial impact of GO and glucose in improving the surface and electrical properties of PEDOT:PSS. The improved photovoltaic performance of the graphene based device was attributed to: a) the insulating properties of glucose which changes the surface wettability and induces the homogeneous deposition of the upper PEDOT:PSS layer and b) the presence of reduced GO sheets restores and improves the electrical conductibility of the film. The hybrid GGO-PEDOT nanocomposite results in outstanding acquired $V_{oc}$, minimizing recombination losses, increase hole-selectivity, and reduced trap density at the PEDOT:PSS along with optimized MAPbI$_3$ coverage. All the improvements
the authors have been introduced, are reflected to the higher PCE of the graphene based device compared to the reference (37% higher PCE).

Planar PSCs demonstrated several advantages compared to the mesoscopic ones: simpler architecture, low temperature processing (below 150 °C), solution processability and thus compatible with printing electronics protocols. The primary characteristics of the HTL should be (1) high hole mobility; (2) compatible HOMO energy alignment with the VB of the perovskite active layer; (3) sufficiently solubility & film formation properties; (4) high transparency; and (5) low cost. E. Jokar et al. proposed the testing of rGO nanosheets, with three different reagents (hydrazine (rGO-NH), sodium borohydride (rGO-BH) and hydrazine benzenesulfonic (rGO-HBS)), as HTL candidates in planar inverted PSCs (ITO/rGO/MAPbI3/PCBM/Ag). The proposed HTL do not suffer from the PEDOT:PSS drawbacks (electrical inhomogeneity, great acidity and hygroscopic properties). This work has clearly demonstrated the importance of the reduction reagent to the overall performance of the PSCs. The authors very clearly demonstrated that the reduction reagent strongly affects (1) the charge transfer from the perovskite layer into the HTL; (2) the stability of the device; (3) the homogeneity of the HTL coverage of the ITO. The best-performed device, deposited onto ITO, was the rGO-HBS based one with PCEs close to 16.4 % (ΔPCE ~ 11% in respect to PEDOT:PSS based PSCs) (see Figure 11a); whereas the record PCEs close to 13.8% onto flexible PEN substrate (see Figure 11c&d), were demonstrated by the rGO-NH based cells that retained 70% of the original device performance after continuous bending for more than 150 cycles (see Figure 11 e&f). The superior performances of the rGO based devices were reflected from the higher acquired $J_{sc}$ and $V_{oc}$ values compared with the corresponding ones in PEDOT:PSS based PSCs. The rGO-HBS based, unencapsulated PSCs demonstrated the higher enduring stability under operating conditions and under 30% of humidity & at 25 °C; the rGO-HBS based PSCs retained the half of their initial performance after 1000 hrs of operational conditions whereas the PEDOT:PSS cells degraded rapidly after 650 hrs (see Figure 11 b).

The HTL building block in p-i-n PSCs (planar inverted) (1) affects crucially the morphology and the crystallization of the top deposited perovskite film; (2) regulates the transmission of the incoming solar irradiation towards the active layer; (3) determines the electronic properties (i.e. hole charge extraction from the perovskite layer towards the HTL) in the HTL/Perovskite interface; and (4) affects the stability of the device (i.e. can filter out the
harmful for the perovskites UV light, it can operate as a shielding against the moisture for the Perovskite). Q. D. Yang et al.\textsuperscript{94} proposed thermally rGO as one of the most promising materials to be used into the planar inverted PSCs. rGO is simply fabricated, is highly transparent, is hydrophobic, has high electron & hole mobilities, adopts low cost fabrication & deposition techniques. Key elements for the rGO success, were the optimization of its thickness in order to balance the WF and its conductivity properties. The application of the rGO as HTL resulted in high performance, PCEs > 16%, and ultra-stable planar inverted PSCs. The higher PCE was attributed to the higher charge extraction rate from the perovskite active layer towards the HTL (PL, TRPL measurements). Whereas the higher shelf time stability and reduced light soaking effects in respect to the PEDOT:PSS based PSCs, were attributed to the improved morphology & crystallization the GO induced into the top deposited perovskite active layer. More particularly encapsulated cells under steady state operation in ambient conditions were characterized for theirs PCE. Then stored under dark conditions. The PCE of the PEDOT:PSS cells dropped by 40% after the elapse of 1400 hrs. In comparison the performance of the rGO cells remained intact (a 10% drop) even after the elapse of 2000 hrs.

Towards the commercialization of the PSCs there are still few obstacles to be overcome i.e. (1) to lower the cost of the overall device by skipping from metal electrodes to carbon tape electrodes; and (2) to enhance the stability of these devices under operational conditions in ambient atmosphere. K. Ahmad et al.\textsuperscript{95} addressed the aforementioned priorities by the utilization GO as HTL in order to prolong the stability of PSCs and the employment of low cost and facile deposited carbon based tape as cathode electrode instead of high cost metal contacts (Ag/Au) or (ZnO/Au). The authors applied their ideas on planar inverted PSCs (ITO/GO/PEDOT:PSS/MAPbI\textsubscript{3}/PCBM/Carbon Tape) and concluded that the incorporation of the GO layer induced the higher photovoltaic performance of the device in respect to the pristine device (GO free) by 147% (the PCE enhanced from 2.1% to 5.2%). This enhancement was attributed to several parameters, (1) the better energy alignment between the active layer and the HTL; (2) the higher hole mobility & higher electron blocking characteristics of the HTL; (3) the superior morphology (homogeneous deposition, lower roughness) induced to the top deposited MAPbI\textsubscript{3} layer; (4) the better induced perovskite crystallization that resulted in larger perovskite crystal grain sizes. Moreover the use of GO under optimization of its thickness, prolonged the stability of the device mainly due to the isolation of the MAPbI\textsubscript{3} crystal from the acidic &
hydrophilic PEDOT:PSS. XRD measurements revealed that the prior the optimization of the GO thickness due to interaction between the MAPbI₃ and the PEDOT:PSS. This interaction led to the MAPbI₃ decomposition after 96 hrs of storage under atmospheric conditions.

The PSCs are facing air and thermal stability issues that lower their performance and jeopardize their commercialization despite their outstanding physical, optical and mechanical characteristics. This makes the stability issues of the PSCs an open challenge that should be addressed urgently. X. Hu et al.96 opened the possibility of using 2D materials as an effective blocking layer towards manufacturing ultra-stable PSCs. More particularly the authors proposed the insertion of a single layer CVD fabricated graphene film between the HTL and the top metal electrode in order to slow down the degradation rate of a normal planar PSCs due to thermal stressing (resulted in perovskite active layer decomposition or the migration of metal atoms from the top electrode into the perovskite layer) and moisture ingress (see Figure 11 g). The CVD graphene layer due to its hydrophobic nature, high impermeability even to the smallest molecules, metal blocking capabilities and its excellent electrical properties, contributed to the enhancement of the air and the thermal stability of the PSCs. The insertion of the graphene layer between the top metal electrode and the HTL had a much stronger impact to the air & thermal stability of the PSCs than to its PCE. The latter remained almost unchanged (Graphene based PSCs demonstrated PCE ~ 15.7% whereas the free of Graphene cells exhibited PCEs ~ 16.6%) (see Figure 11 h) after its exposure to ambient environment with 45% humidity; in contrary the air and thermal stability of the Graphene based cells increased substantially in respect to the corresponding figures of the Graphene free cells. The air stability of non-encapsulated Graphene based PSCs remained almost intact under ambient conditions (45% of Humidity) since they kept 95% of their initial PCE after 96 hrs of exposure to ambient conditions. On the other hand similar Graphene free PSCs degraded for the same period to the 57% of their pristine PCE values (see Figure 11 i). This evident degradation was due to the CH₃NH₃PbI₃ decomposition due to moisture filtration. Moreover the thermal stability of the graphene based devices were superior in respect to the reference cells. The former kept the 96% of its initial PCE after annealed at 80 °C, in a glovebox for 12 hrs whereas the latters’ PCE degraded severely by 54% for the same thermal treatment. This degradation was mainly attributed to the Au metal diffusion into the perovskite from the top electrode. This diffusion formulated shunts across the device, reducing all of its photovoltaic parameters after annealing treatment (see Figure 11 j&k).
H. Guo et al.\textsuperscript{97} demonstrated the use of a composite HTL build by PEDOT:PSS and solution processed sulfated GO (sGO). The build planar inverted MAPbI\textsubscript{3} PSCs exhibited superior efficiencies in respect to PEDOT:PSS cells by more than 20\% (the PCE improved from 11.5\% to 13.9\%). The observed enhancement was attributed to many parameters, (1) the lower $R_s$ of sGO compared to the insulating GO films; (2) the higher hole extraction from the perovskite active layer; (3) the higher transmittance the sGO/PEDOT:PSS composite characterized in 1:1 concentration ratio; (4) the improved wettability the sGO offers the PEDOT:PSS that allowed the more uniform deposition onto ITO coated glass; (4) the more uniform deposition and thus better electrical contact of the perovskite layer onto the HTL; (5) the larger perovskite grain sizes fabricated. Moreover the improved PCE, the employment of the sGO/PEDOT:PSS composite under optimum volume concentration, reduced the hysteresis phenomena these devices demonstrated from 17.4\% to 6.5\% deviation (reverse compared to the forward scan).

One of the objectives in the research of hybrid PSCs, is the achievement of the theoretical limit values of the open circuit voltage (1.32 V). Until now, a large proportion of the output voltage remains much below $\sim$ 1.2 V. Improvement of the engineering of interfaces between perovskite active layer and the charge transporting layers is the key strategy to achieve this objective. It has been reported that the main contributor in energy loss in metal halide PSCs is the recombination of charge carriers due to trap states at grain boundaries and surfaces as well as point defects such as interstitial defects or vacancies in the perovskite crystal lattice. To reduce the charge carrier recombination, surface modification has become one of the most powerful tools to minimize the losses and thus increase the $V_{oc}$ without sacrificing $J_{sc}$ and FF in PSCs. H. Li et al.\textsuperscript{98} utilized a functionalized rGO with a small molecule 4-Flurophenyl-hydrazine hydrochloride (4FPH) as a interfacial layer in order to passivate the traps (e.g. under-coordinated Pb ions and Pb clusters) on the surface and at the boundaries of MAPbI\textsubscript{3-$x$}Cl\textsubscript{$x$}. Their findings pointed out the $V_{oc}$ losses can be largely reduced via passivation the under-coordinated Pb ion traps. The addition of the 4FPH molecule had no effect in formation of perovskite and the following HTL (Spiro-OMeTAD). The trap passivation benefited the faster charge extraction from the perovskite into the HTL. This clear indication of the rGO-4FPH better-induced interface engineering, was reflected to the substantially enhancement of the acquired $V_{oc}$ (increased from 1.03 to 1.11 V) in respect to rGO-4FPH free PSCs. The higher PCE of the rGO-
4FPH based cells compare to the control devices by 20.34% (record PCE of 18.75%), was mainly attributed to the higher $V_{oc}$ values (by 7.76% mainly due to traps passivation) than the higher obtained values of $J_{sc}$ (increase by 6.9%, mainly due to faster extraction rates) and of FFs (increase by 4.7%, more efficient collection). Moreover the inclusion of the rGO-4FPH interlayer showed that the traps passivation can also slow down the light activated degradation processes; the rGO-4FPH based cells showed higher stability while stored under constant one-sun illumination in N$_2$ filled glove box.

The significant advances in PCEs of PSCs should be accompanied by one additional achievement regarding the demonstrated environmental stability by these devices. One way to meet this objective is through the construction of charge transport layers (or otherwise known as interfacial layers) that minimize the charge recombination rates and facilitate their collection in the respective electrodes. The characteristics that such materials should have are high transparency, high conductivity, charge selectivity, well matched energy levels with them of the perovskite and chemical stability. C. H. Jung et al. explored the advantages of GO and reduced rGO, such as (1) suitable work function (GO, 4.7 – 4.9 eV); (2) high hole conductivity (rGO) and at the same time tackled theirs disadvantages such as (1) low charge transport capability (GO); (2) lower dispersibility (rGO); and (3) smaller WF (from 4.5 to 4.7 eV). The authors proposed the utilization of a polyacrylonitrile (PAN) grafted rGO hybrid as a stable HTL in high performance planar MAPbI$_3$ PSCs. The combination of the qualities of the proposed HTL such as solution processablity, formation of uniform & smoother thin film morphology, good conductivity (0.87 S/cm), high WF (4.87 eV), converts it more attractive than other interfacial materials used (e.g. PEDOT:PSS, chemical converted graphene nanoflakes) and lead to higher achieved PCEs (~ 9.7%) and lifetimes. The better weather stability of the PRGO HTL based devices in respect to the hydrophilic PEDOT:PSS was ascribed to its highly resistant to moisture.

Z. Zhou et al. proposed the incorporation of a bilayer made of rGO and PTAA as HTL in planar inverted MAPbI$_3$ PSCs. The tested HTL demonstrated the advantages of both rGO and PTAA: (1) long-term light soaking stability (rGO); (2) UV filtering ability (rGO); (3) film forming ability (PTAA); (4) hydrophobicity (PTAA); and (5) appropriate energy alignment between the VB of HTL and the VB of MAPbI$_3$ absorber. As a result of the aforementioned HTL bilayer characteristics, faster hole extraction rates from the perovskite active layer towards the bilayer HTL, superior quality MAPbI$_3$ crystals and better interfacial morphologies were
achieved. PSCs fabricated on glass/ITO showed PCEs of 17.2%. Moreover, sealed PSCs exhibited high stability, retaining ~ 90% of the initial PCE after 500 hrs of light soaking.

R. Zhang et al.\textsuperscript{101} utilized graphene sheets – functional carbon nanotubes (graphene:f-CNTs) composite as low cost, solution processed HTL in planar inverted MAPbI\textsubscript{3} based PSCs. As a result of the better induced MAPbI\textsubscript{3} absorber crystallization, the improved interface engineering between the perovskite active layer and the HTL, the higher hole conductivity the insertion of the f-CNTs secured and the hydrophobic nature of the graphene:f-CNTs, compared to the PEDOT:PSS based reference HTL, resulted in a 16.5% enhancement in PCE (from 12.7% to 14.8%) and prolonged lifetime. More precisely, the unencapsulated PSCs with graphene:f-CNTs as the HTL, maintained 80% of their initial PCE whereas the PEDOT:PSS devices have completely degraded after 48hrs of storage at 35 °C and 20% humidity conditions.

J. C. Yu et al.,\textsuperscript{102} showed a highly efficient and stable inverted PSC by introducing a PEDOT:GO composite film as HTL. The inverted PSCs with an optimized PEDOT:GO composite film exhibited a record PCE of 18.09%, which is by 21% higher than that of the pristine PEDOT:PSS based device. The high PCE of the graphene based device was attributed to: a) the superior properties of the PEDOT:GO composite film; b) higher optical transmittance; c) superior electrical conductivity and higher work function; d) longer perovskite grain size and e) suppressed leakage current. The higher PCE was due to the improved carrier extraction and \( V_{oc} \) of the device. The authors highlight, the enhanced long term stability of the PEDOT:GO PSCs compared to the reference device.

In summary the incorporation of graphene based HTLs can vastly contribute to the improvement of mesoscopic and planar PSCs performance. More particular the control of the graphene HTL’s thickness can balance (1) the electron & holes mobilities within the device and thus boost the device performance (by reducing the recombination rate); (2) the hole transfer from perovskite active layer into the HTL (revealed by the level of the PL quenching). Also in the case of the planar inverted architecture, the graphene based on HTLs facilitated the faster and better crystallization of perovskite crystals (larger crystal domains and more uniform & larger coverage ratio of the perovskite film) onto them compared to the respective characteristics when PEDOT:PSS employed. Apart of the larger coverage of the perovskite film when graphene based HTL is employed, the enhanced roughness the perovskite on the GO exhibited results in the more efficient light trapping the corresponding cells demonstrated compared to the PEDOT:PSS
PSCs. Furthermore GO or rGO can be utilized as an interlayer between perovskite semiconductor and the HTL or the HTL and the metal electrode, improving the interfaces and thus leading to higher PCEs and prolonged the operational lifetime of these PSCs due to the shielding protection against moisture and water molecules the graphene provides to the perovskite active layer.

**Figure 11.** (a) PCEs with standard deviations of PSCs with the HTLs. (b) Lifetimes of the PSCs with HTL made of PEDOT:PSS, GO, and rGO-HBS as a function of storage period. (c) J-V curves and (d) EQE spectra of flexible PSCs made of GO, rGO-NH, and rGO-HBS as HTL. (e) Image of the bending experiments performed with the flexible PSCs bent to a tube of radius 5 mm. (f) Normalized PCE of flexible PSCs as a function of bending cycles.

Reproduced with permission from Ref. 91 (Copyright© 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim); (g) Schematic of the blocking effect of CVD graphene in a normal planar architecture PSC. (h) J-V curves and (i) Normalized PCE of PSC with or without the CVD graphene blocking layer after ageing in air for different times. Nyquist plot of PSCs with (j) and without (k) the CVD graphene blocking layer after ageing in air for 96 h. Reproduced with permission from Ref. 94 (Copyright© 2017, The Royal Society of Chemistry)

**Table 3.** Summary of the record results of graphene based HTLs in mesoporous & planar PSCs.

<table>
<thead>
<tr>
<th>Architecture / Absorber</th>
<th>HTL</th>
<th>PCE (%)</th>
<th>Other Benefits</th>
<th>APCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
</table>

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<table>
<thead>
<tr>
<th>Material System</th>
<th>Description</th>
<th>Moisture/Light Stability</th>
<th>Long-Term Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>TSHBC /nanographene composite</td>
<td>14</td>
<td>15 (spiro-OMeTAD)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>GO at the interface between AL and HTL (Spiro – MeOTAD)</td>
<td>15.1</td>
<td>N/A</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>rGO / dopant free Spiro - OMeTAD</td>
<td>10.6</td>
<td>59.14 (dopant free Spiro OMeTAD)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>rGO</td>
<td>6.62</td>
<td>-56 (Spiro – OMeTAD)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>SWCNTs / GO /PMAA composite</td>
<td>11.7</td>
<td>-3 (Spiro – OMeTAD)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>rGO – PhOMe/P3HT composite</td>
<td>9</td>
<td>38 (P3HT)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>P3HT/F-Graphene composite</td>
<td>13.82</td>
<td>69 (P3HT)</td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Amino Functionalized rGO</td>
<td>14.6</td>
<td>N/A</td>
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<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CuBuPc / GO bilayer</td>
<td>14.4</td>
<td>N/A</td>
</tr>
<tr>
<td>Mesoscopic / CsFAMAPbI&lt;sub&gt;3&lt;/sub&gt;Br&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CuSCN / rGO</td>
<td>20.2</td>
<td>-1.5 (spiro – OMeTAD)</td>
</tr>
<tr>
<td>System Description</td>
<td>Details</td>
<td>Ambient Stability</td>
<td>Bending Tolerance</td>
</tr>
<tr>
<td>--------------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃ₓClₓ</td>
<td>GO (2 nm thick, spin coating thin film)</td>
<td>12.4</td>
<td>N/A</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>rGO</td>
<td>10.8</td>
<td>18 (PEDOT:PSS devices)</td>
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<tr>
<td>Planar Inverted / MAPbI₃ₓClₓ</td>
<td>PEDOT:PSS:AgOTf-doped GO</td>
<td>11.90</td>
<td>11.2 (PEDOT:PSS)</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>rGO/PEDOT:PSS</td>
<td>10.6</td>
<td>N/A</td>
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<tr>
<td>Planar Inverted / MAPbI₃ₓClₓ</td>
<td>PEDOT:PSS / GO-NH₃</td>
<td>16.1</td>
<td>33 (PEDOT:PSS)</td>
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<td>Planar Inverted / MAPbI₃</td>
<td>PEDOT:PSS - UV reduced GO</td>
<td>7.29</td>
<td>N/A</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>GO/PEDOT:PSS</td>
<td>13.1</td>
<td>30 (PEDOT:PSS)</td>
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<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>oxo – functionalized graphene</td>
<td>15.2</td>
<td>Long-term stability under</td>
</tr>
<tr>
<td>Device Type</td>
<td>HTL</td>
<td>AM 1.5 G illumination</td>
<td>Long-term Stability</td>
</tr>
<tr>
<td>-----------------------------</td>
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<td>-----------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>GGO-PEDOT</td>
<td>12.8</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>rGO nanosheets</td>
<td>16.4</td>
<td>Ambient</td>
</tr>
<tr>
<td></td>
<td>Thermally reduced rGO</td>
<td>16.5</td>
<td>Ambient</td>
</tr>
<tr>
<td></td>
<td>GO/PEDOT:PSS composite and Carbon Tape electrode</td>
<td>5.2</td>
<td>Ambient</td>
</tr>
<tr>
<td>Planar Normal / MAPbI₃</td>
<td>CVD Graphene between top electrode &amp; HTL</td>
<td>15.7</td>
<td>Air and thermal</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>sGO - PEDOT:PSS</td>
<td>13.9</td>
<td>N/A</td>
</tr>
<tr>
<td>Planar Normal / MAPbI₃Clₓ</td>
<td>rGO – 4FPH/spiro – OMeTAD</td>
<td>18.75</td>
<td>Improved</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI₃</td>
<td>PAN-grafted RGO (PRGO)</td>
<td>9.7</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Graphene-Perovskite Hybrids based PSCs

Morphology, grain size and thickness of the employed perovskite semiconductor films are key factors that contribute to high PCEs. The control of the nucleation & crystallization rate and the passivation of the charge trap states of the perovskites and corresponding grain boundaries, are strategies towards the secure of high PCEs. Table 4 summarizes the record results that have been reported in the literature regarding the utilization of GRMs into the perovskite layer of mesoporous and planar PSCs.

| TABLE 4 |  |  |  |  |  
|---|---|---|---|---|---|
| Planar Inverted / MAPbI₃ | r-GO/PTAA | 17.2 | Flexibility | 12 | (PTAA) |
| Planar Inverted / MAPbI₃ | graphene:f-CNTs | 14.8 | Storage Stability | 16.5 | (PEDOT:PSS) |
| Planar Inverted / MAPbI₃ₓBr₁₋ₓ | PEDOT:GO | 18.09 | Ambient Stability | 21 | (PEDOT:PSS) |

Graphene-Perovskite Hybrids based PSCs

M. Hadadian et al.¹⁰³ suggested the incorporation, of few layers of transparent nitrogen doped graphene oxide (N-RGO) into mixed metal-halide perovskite absorber. As a result, the authors reported the increase of the perovskite grain size (due to the slowing down by a factor of two of the crystallization rate, led to an increase of the Jₛₜ & FF) by 150% (see Figure 12 a-e) and the passivation of the perovskite boundary interfaces by the N-RGO (led to higher Vₒc, see Figures 12 g-i). The SEM images showed that the longer MAPbI₃ grain sizes due to the mixing with the N-RGO, resulted in thinker films (that enhanced also the light harvesting compared of the reference devices). The resulting PSCs exhibited null hysteresis PCE of 18.7% as compared
to the control device with 17.3% (see Figure 12 f), as a result of the larger grain size of perovskite / N-RGO and thus less grain boundaries.

Minimizing the charge recombination at the surface and in the bulk perovskites’ grain boundaries is the most effective strategy to further increase the PCE of the PSCs. The grain boundaries modification at the surface of perovskite can be accomplished by theirs passivation, neutralization of the daggling bonds at the grain boundaries of between perovskite crystals, using graphene or fullerene materials between the ETL and the perovskite absorber. Less work has been reported regarding the respective passivation of the grain boundaries into the bulk of the perovskite. X. Fang et al.\textsuperscript{104} reported the use of GQDs, with diameters of the order of 20 nanometers, in order to deal with recombination that occurs at the grain boundaries into the bulk of perovskites (MAPbI\textsubscript{3}). The authors did not only observe reduction of the recombination rates but also reported facilitation of the electron transfer (the extraction time has been lowered from 1.09 ns to 0.93 ns) from the perovskite layer into the ETL in the case of GQDs based PSCs. The GQDs have dispersed within the perovskite and formulated a composite. TEM images revealed that QDs were mainly decorating the perovskite crystal’s surface. The observed facilitation of electron transfer from the perovskite to the ETL were mainly attributed to the excellent optoelectronic properties of the GQDs (long electron diffusion lengths, fluorescence quantum effect) and the hydrogen bonds established between the GQDs and the MAPbI\textsubscript{3} crystal. The highest efficiency of 17.62% was achieved with 7% GQDs which corresponds to an 8.2% enhancement in respect to a pure perovskite based device. Further increase in the concentration of GQDs into the MAPbI\textsubscript{3} network degraded the PCE due GQDs agglomeration that operated as charge recombination centers.
Figure 12. SEM top-view images of (a) undoped perovskite absorber film and (b) N-RGO doped hybrid perovskite absorber film. (c) Image of perovskite films during crystallization procedure at 100 °C (top undoped and bottom N-RGO doped perovskite films). (d) $^1$H NMR of perovskite solution, and perovskite/N-RGO hybrid solution collected in DMF-d$_7$ (stars represent the peaks of DMF-d$_7$ used as solvent). (e) Magnification of the scale between 8.3 and 9.8 ppm. (f) J-V curves for undoped perovskite and perovskite/N-RGO hybrid PSCs. (g) Average $V_{oc}$ for the undoped perovskite, perovskite/RGO hybrid, and perovskite/N-RGO hybrid PSCs. (h) $V_{oc}$ of undoped, and PSCs with N-RGO layer on top of perovskite in six batches. (i) TRPL decay plots of undoped perovskite, perovskite/RGO, and perovskite/NRGO hybrid films. Reproduced with permission from Ref. 100 (Copyright© 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

Planar PSCs

C. C. Chung et al.$^{105}$ proposed the adoption of bulk heterojunction architecture to address the unbalanced mobility of photo generated carriers within MAPbI$_3$ based PSCs. More specifically, the authors presented a bulk heterojunction setup between MAPbI$_3$ and GO that acted as hole donor and hole acceptor respectively. The impact of the mixing of GO with the MAPbI$_3$ was
multiple and beneficiary since (1) enhanced the charge mobility; (2) enhanced the charge separation; and (3) retarded the charge recombination within the perovskite active layer. In summary the insertion of GO within the perovskite layer facilitated the hole extraction rate since engineered more interfaces, between MAPbI\textsubscript{3}/GO, under an optimum GO concentration (0.05 mg/mL). As a result, an increase of the PCE of approximately 24% was reported, with the PCE reaching values higher than 15% (15.2%) in a planar inverted PSCs (ITO/GO/MAPbI\textsubscript{3}/GO/PCBM/Ag) (See Figure 13 a). In the same study the authors replaced the problematic PEDOT:PSS with GO as the utilized HTL providing higher stability (see Figures 13 b&c).

![Figure 13](image)

**Figure 13.** (a) Histograms of pristine perovskite absorber (PSK) and perovskite absorber doped with GO (PSK:GO) hybrid composite planar inverted PSCs. (b) Profiles of the lifetime of pristine PSK and PSK:GO hybrid composite PSCs as a function of storage period. (c) Nyquist plots obtained from EIS for pristine PSK and PSK:GO hybrid composite PSCs under one-sun illumination and open-circuit conditions.

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In summary the incorporation of GRMs in the perovskite active layer, have mainly an impact on the perovskite fabricated crystal size, passivated more efficiently the interior boundary
regions within the perovskite crystal resulting in faster extraction rates and efficiencies higher than 18%.

**Table 4.** Summary of the record results of graphene based HTLs in mesoporous & planar PSCs.

<table>
<thead>
<tr>
<th>Architecture / Absorber (reference)</th>
<th>Perovskite Absorber</th>
<th>PCE (%)</th>
<th>Other Benefits</th>
<th>ΔPCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoscopic / FA&lt;sub&gt;0.85&lt;/sub&gt;MA&lt;sub&gt;0.15&lt;/sub&gt; Pb(I&lt;sub&gt;0.85&lt;/sub&gt;Br&lt;sub&gt;0.15&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; – N-rGO composite</td>
<td>18.73</td>
<td>N/A</td>
<td>8.2 (free of N-rGO)</td>
<td>M. Hadadian et al. 2016 [103]</td>
<td></td>
</tr>
<tr>
<td>Mesoscopic / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>GQDs - MAPbI&lt;sub&gt;3&lt;/sub&gt; composite</td>
<td>18.34</td>
<td>Ambient Stability</td>
<td>8.2 (free of QDs)</td>
<td>X. Fang et al. 2017 [104]</td>
</tr>
<tr>
<td>Planar Inverted / MAPbI&lt;sub&gt;3&lt;/sub&gt;</td>
<td>MAPbI&lt;sub&gt;3&lt;/sub&gt; - GO</td>
<td>15.2</td>
<td>Storage Stability</td>
<td>23.5 (free of GO)</td>
<td>C.C. Chung et al. 2017 [105]</td>
</tr>
</tbody>
</table>

**Conclusions and outlook – future milestones**

Metal halide PSCs have become the new sensation in PV devices and the most promising new technology in academia and industry. Their evolution within few years is impressive and faster than any other solar technology experienced until now. Due to their physical and electrical properties and their astounding technical advantages, such as solution processability, compatibility with flexible substrates and abundance of ingredients have resulted in new impressive beyond solar cell applications such as sensing, lighting. Although their impressively high efficiencies, PSCs face challenges that should be overcome, mainly regarding their stability and scalability, in order to elevate market realization and become an alternative to silicon based solar cells.

The major challenges PSCs should address in the near future in order to become a mass used commercial product, include (1) further enhancement of their photovoltaic performance &
stability; (2) controllable thin film growth & deposition; (3) scalability; (4) low toxicity; and (5) lower cost.\textsuperscript{109,110} The PCE of PSCs since 2015 seems to be stacked in certified performances of the order of little bit higher than 22%. To surpass 22% more work has to be done to improve $V_{oc}$ and FF. One-way to be achieved this goal is to improve the kinetic dynamics of the transport of the photo-generated carriers by improving the interface engineering of various layers in PSC devices.\textsuperscript{111} In most cases the reported high PCE referred to lab scale devices ($\sim 0.1 \text{ cm}^2$). The first issue to be emphasized is the need to develop fabrication methods than enable high performance on large-scale perovskites solar modules. The highest reported PCE in this scale ($\sim 100 \text{ cm}^2$) is 4.3%.\textsuperscript{112} The scientific community should be focused to identify the internal and external degradation mechanisms in this kind of solar cells. Fully control and understanding of the crystallization process and which physical parameter affects this crystallization process should be realized in order to build more efficient and reproducible devices. The role of grain boundaries on recombination process is still debatable. The development of other deposition techniques such as spray coating should be optimized to be able to build large area cells with the PCE of the small illumination area devices; stability issues originating from water molecules interaction with the perovskite, thermal loading management, light soaking and hysteresis effects should be tackled; ITO or FTO free PSCs should optimize their performance; flexible PSCs should reach the performance of the rigid substrate based PSCs; the charge carrier recombination should be tailored; and lead free PSCs should enhance their PCEs to the level of the lead based PSCs.

A lot of strategies have been suggested to address all these challenges such as the collaboration of hybrid PSCs with metal and up conversion nanoparticles,\textsuperscript{113} with other 2D materials,\textsuperscript{114} with graphene and GRM, the development dual source evaporation or sequential deposition processes,\textsuperscript{115,116} the choice of solvents, concentrations and processing additives\textsuperscript{117}, and the introduction of anti-solvent approaches.\textsuperscript{118} The inclusion of graphene and GRMs within the different building blocks of PSCs is a very promising approach and this is revealed from the number and impact of publications and the recently published results. This incorporation is one of the most successful approaches to tackle many of the aforementioned PSCs challenges. Graphene based PSCs seem to address all the challenges towards the enhancement of their potential for commercialization of this technology. These GRMs have played various roles such as electron/hole transport layers, top contacts and
interlayers, within PSC setups. The incorporation of graphene and GRMs e.g. GO, rGO or functionalized GO has significant advantages: (1) improves the PSCs stability under dark and operational conditions, contributing to the achievement of degradation rates of the order of 0.25 – 0.5% losses per year; (2) encourages the better crystallization preferred orientation, longer crystal grain sizes, few pin holes of the perovskite crystal at low temperatures; (3) supports more uniform deposition of perovskite films onto graphene based transport layers (the latter have the role of the deposition substrate for the perovskite absorber); (4) induces sufficient surface coverage of the perovskite film; (5) improves the morphology (less roughness) of the top deposited perovskite film; (6) enhances the wettability of the materials that are deposited onto the graphene films, either are hole transport or electron transport materials; (7) facilitates the charge extraction from the perovskite active layer towards the HTL& ETL building blocks; (8) facilitates the faster transfer of holes and electrons when graphene based interlayers are inserted between the ETL and HTL respectively and the corresponding electrodes; (9) promotes the charge blocking abilities of the interlayer in which it is incorporated; (10) builds high conductive, transparent & flexible TCEs; (11) retards or even stops a lot of the extrinsic degradation mechanisms related to metal intrusion into the perovskite in high temperatures contributing in improved stability performances; (12) shields the perovskite from the harmful UV or moisture/water to reach it; and (13) makes less pronounced the hysteresis.

The synergy of graphene and perovskite is challenging but has highly significant results because it combines the superb properties of the two materials: abundance, low cost, compatibility with low temperature solution processing and printing techniques, excellent electrical, mechanical and optical properties and large scale production potentials. However, the incorporation of GRMs as a TCE or within the interlayers of PSCs is a technology that despite its progress and encouraging results still faces some challenges. A lot of mechanisms are still unclear and thus there is no a state of the art PSC designs that meets commercial applications standards. The first challenge is to further reduce the extraction times from the perovskite active layer into the ETL compared to the reported hot carrier thermalization extraction times. This is expected to enhance the PSCs PCE by reducing the recombination rates. Key parameter in this effort may be the enhancement of the demonstrated conductivity of the incorporated GRMs (mainly through its functionalization with atoms of higher electronegativity or with its doping with oxide coated metal nanoparticles). At the same time the restoring of GO conductivity or its n-doping requires high temperatures that
could degrade the perovskite that is deposited below in the case of inverted PSCs. This means that controlled experiments are necessary to be implemented in order to address some innovative process protocols. Another important issue to be investigated further is the lowering of the FF when graphene builds nanocomposites with the SrTiO$_3$ that are employed as ETLs. A most like reasoning of this is the formation of recombination centers but further studies have to be done. Since the PCEs of the rGO / TiO$_2$ layers device are much lower than the highest reported, more work in needed on the optimization of the atomic layered deposited bl-TiO$_2$ and mp-TiO$_2$ thickness. Future direction linked with the impact of GO based HTLs could be the further study of the HTL thickness regarding hysteresis and light soaking effects. Also, even though all the photovoltaic characteristics of the PSCs were very much affected by the thickness of the employed GO HTL, the $V_{oc}$ remained close to one V. The reasoning behind this stable behavior needs to be elaborated further. Another important task that needs more investigation is to identify the physical & chemical properties of the graphene based HTL that affect significantly the crystallization process of the top deposited perovskite films (particular in the planar inverted set up). This is a very crucial task to be studied since the morphology and possible interfacial chemical changes of perovskite films and the HTL determine the performance of the PSC device. The lower performance of the graphene – based HTLs, instead of the spiro-OMeTAD, and ITO/FTO free PSCs should motivate future studies towards the building of efficient top/bottom graphene based electrode & HTL PSCs. Even though there are reports that state that the hysteresis phenomenon is less obvious in planar inverted graphene based PSCs (mainly due to the faster charge extraction rates and the more balanced mobilities between electron and holes in graphene based cells), the physics behind these reports is still unclear and not well supported. More theoretical and experimental work has to be devoted to reply this challenge. Another challenge is the fabrication of large-scale solution processed graphene based PSC solar modules with optimized photovoltaic PCE. The fabrication and deposition of solution-processed graphene in large scales is still a non solved challenge. The majority of the work reported related the GRM based PSCs, has been implemented with MAPbI$_3$ absorber. Almost no work has been done in GRM involvement in perovskite semiconductors with energy band gaps between 1.1 and 1.4 eV that are ideals for harvesting more solar energy. These systems are building by mixing halides or making Sn-Pb compounds and have not reached their Shockley – Queisser limit. This gives plenty room to graphene and GRMs to be engaged and be studied. Moreover little work has also
been done regarding the GRM based FAPbI$_3$ systems. The latter have become a major avenue for research because of the higher demonstrated thermal stability and its narrower bandgap. One of the most significant issues concerns the investors, fabricators is the toxicity of lead used in PSCs. This represents a huge pollution source in manufacturing and disposal phases. It is expected that a lot of emphasis will be given to lead free PSCs. This is another opportunity window for the GRMs to be involved and research to be done, how this family of PSCs PCEs can be improved as a result of its synergy with GRMs. In future should be studied how GRM e.g. HTL affects the phase stabilization and if it degrades the segregation of perovskites in this family of PSCs. The contribution of GRMs into the more efficient thermal management of PSCs during their testing or during their operation where the temperatures are above 60 °C should be studied further. The excellent thermal properties of graphene and its incorporation within the perovskite active layer (e.g. in the form of GQDs) or the transport layers, is expected to slow down the impact of this extrinsic degradation factor. The use of graphene-based electrodes also should eliminate the degradation effect induced in high temperatures with the mitigation of metal electrode ions into the perovskite active layer. Moreover the impact of GRMs to dynamics of lattice deformation and hence halide migration during PSCs aging and thermalization, has not been extensively studied. It is must be noted that hysteresis$^{120}$ and reversible losses$^{121}$ contribute to fast and slow device degradation respectively. A comprehensive study of the impact of GRM based electrodes on the reversible losses and the accumulation of ions at interfaces on different PSC architectures is still lacking.

Universal fabrication protocols regarding the PCE optimization as a function of the thickness of GRM layers are still absent. The processing protocols should be synchronized with in situ characterization techniques such as X-ray scattering and spectroscopy in order to optimize the processes within a PSC e.g the kinetic dynamics of the photo-generated carriers as a function of the GRM layers thickness.

The promising prospects of flexible PSCs in high profile applications such as flexible optoelectronic devices, building integrated PVs (BIPVs) have placed high demands in the fabrication of low temperature semitransparent PSCs. In order to promote the competitiveness of these flexible solar cells the boosting of their PCE should be intensified. New high performed substrates and low temperature processed interlayers should be introduced that will elevate flexible PSC PCE above the 15% nowadays reported performances. Moreover the performance
of large – area (in case of BIPV) PSCs is very much dependent on whether the perovskite and the incorporated GRMs (in case of GRM based PSCs) deposition techniques enable controlled growth and deposition of high quality layers over large areas in low cost. Regarding graphene, the lowest cost deposition method, the spin coating, is not characterized by the best graphene quality that can provide even in small deposition areas. A lot of research has to be implemented in improving the low cost deposition of GRMs over large areas.

The GRMs based metal halide PSCs is a technology that exhibits high efficiencies (> 20%), even though there are no certified results yet, lower costs (solution processability), reproducibility (make the hysteresis effects less pronounced), stability (for several days under operational conditions), that are paramount characteristics for a new technology to be established. The aforementioned challenges and future perspectives should be addressed with the introduction of more well defined processing and stability protocols that have a more universal than individual character.

**Conflict of interest**

There are no conflicts to declare.

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**Abbreviations of the different GRMs**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CVD Graphene</td>
<td>Chemical Vapor Deposited Graphene</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>N-RGO</td>
<td>Nitrogen Doped Reduced Graphene Oxide</td>
</tr>
<tr>
<td>SGO</td>
<td>Sulfated Graphene Oxide</td>
</tr>
<tr>
<td>CQDs</td>
<td>Carbon Quantum Dots</td>
</tr>
<tr>
<td>GQD</td>
<td>Graphene Quantum Dots</td>
</tr>
<tr>
<td>3DHG</td>
<td>3D honeycomb structured graphene</td>
</tr>
<tr>
<td>MG</td>
<td>Multilayered Graphene</td>
</tr>
</tbody>
</table>
SG  Single Layer Graphene
LPE Graphene  Liquid Phase Exfoliated Graphene
GO-Li  Lithium Neutralized Graphene Oxide
rGS  Reduced Graphene Scaffold
EFGnPs-F  Fluorine Functionalized Graphene Nano Platelets
F-Graphene  Functional Graphene
NGs  amino functionalized rGO
NGONRs  nitrogen doped graphene oxide nanoribbons
AgOTf-doped GO  silver trifluoromethane sulfonate doped GO
GO:NH$_3$  ammonia modified graphene oxide
UV rGO  Ultra-violet reduced graphene oxide
oxo – G1  oxo – functionalized graphene
rGO – 4FPH  reduced graphene oxide functionalized with 4-Flurophenyl-hydrazine hydrochloride
PAN grafted rGO  polyacrylonitrile grafted reduced graphene oxide

Notes and references

1 International Energy Agency Photovoltaic Power Systems Programme, iea-pvps.org
22 F. Schwierz and Nat. Nanotechnol., 2010, **5**, 487–496.


